Solid-State Models of Ion Solvation: Crystal Structures of Dimethyl Sulfoxide Solvates of Alkaline Earth Cations

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Structural studies of the dimethyl sulfoxide solvates of the perchlorates of Mg, Sr and Ba show the presence of a variety of complex ion species indicative of the forms possible in solution. While $Mg(ClO_4)_2{\cdot}6dmso$ contains the expected $[Mg(dmso)_6]^{2+}$ cation, the crystallised strontium species contains a mononuclear $[Sr(dmso)_6]^{2+}$ cation and two dinuclear species, the complex $[(dmso\text{-}O)_5Sr(\mu\text{-}dmso\text{-}O)_3Sr(OH_2)(dmso\text{-}O)_3]^{4+}$ containing both seven- and eight-coordinate Sr metal centres, and $[\{(dmso\text{-}O)_5Sr(\mu\text{-}dmso\text{-}O)\}_2]^{4+}$ containing seven-coordinate Sr metal centres. The barium complex, of empirical formula $Ba(ClO_4)_2{\cdot}5dmso$, contains a centrosymmetric dimer, $[Ba_2(dmso\text{-}O)_6(\mu\text{-}dmso\text{-}O)_4(O_2ClO_2)_2]^{2+}$, involving an unsymmetrically chelating perchlorate and a nine-coordinate Ba metal centre.

Introduction

In the sense that they are the end products of solvent removal from solutions, crystals and the species they contain may provide an indication of the species dominant in the most concentrated of solutions. In many instances, there is good evidence that the species characterised in crystalline solids are those predominant in relatively dilute solutions, though there is also evidence to the contrary.[1] At the very least nonetheless, species found in the solid state illustrate possible forms for solution species and, especially for elements which are either spectroscopically silent or inconveniently studied by spectroscopic methods, single-crystal X-ray diffraction measurements can provide by far the most efficient means of precisely defining the nature of the forms that dissolved solutes may take. This is particularly true for many metal derivatives, Sc^{III} providing an intriguing example,[2] and the case of $Pb(ClO_4)_2$ solvation by dimethyl sulfoxide (dmso) providing an example[3] of how seemingly simple stoichiometry may disguise some quite surprising coordination chemistry. In conducting an extensive structural study of solvated metal salts, we have found that dmso solvates of the alkaline earth cations provide remarkable examples of how complicated the nature of such solvates may prove to be.

Results and Discussion

Analytical characterisation of the recrystallised dmso solvates of the perchlorates of the alkaline earth metals is close to consistent with their formulations as $Be(ClO_4)_2{\cdot}4dmso$[4] $Mg(ClO_4)_2{\cdot}6dmso$, $Ca(ClO_4)_2{\cdot}6dmso$, $Sr(ClO_4)_2{\cdot}6dmso$ and $Ba(ClO_4)_2{\cdot}5dmso$. Given the knowledge that in numerous complexes of quite diverse ligands, the coordination number of Ba^{II} invariably equals or exceeds that of Sr^{II} in its direct analogue,[5] this fact alone indicates that some of these formulae may be oversimplified representations. In fact, this is not so for the Mg complex, for which the structure determination (Figure 1) provides a justification for its description as $[Mg(dmso\text{-}O)_6][ClO_4]_2$.

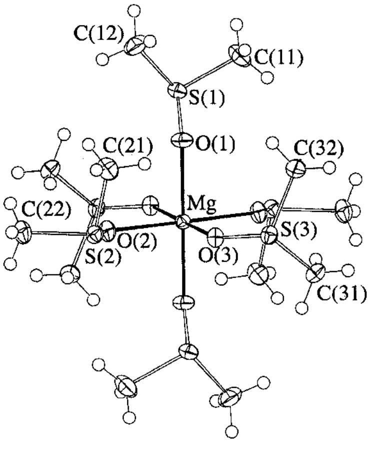

Figure 1. Projection of the centrosymmetric $[Mg(dmso\text{-}O)_6]^{2+}$ cation present in solid $Mg(ClO_4)_2{\cdot}6dmso$; Mg−O(1,2,3) are 2.063(1), 2.084(1), 2.0512(9) Å, the maximum angular excursion from orthogonality being 88.60(4)°; Mg−O−S angles are 130.18(5), 127.51(7), 139.80(7)°

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Although our numerous efforts to obtain crystals of both the Be and Ca complexes suitable for a structure determination have proved fruitless, so that strictly speaking the nature of the solid perchlorate species must be considered unknown, there would appear to be little doubt that the Be compound should contain tetrahedral [Be(dmso-*O*)$_4$]$^{2+}$ [4,6] while the octahedral [Ca(dmso-*O*)$_6$]$^{2+}$ species has been structurally characterised in association with two different anions.[7] The remaining two members of the alkaline earth series, however, provide some surprises. The Ba compound, which proves to have the "simpler" solid-state structure, is best formulated as the dimer [Ba$_2$(dmso-*O*)$_6$(μ-dmso-*O*)$_4$(O$_2$ClO$_2$)$_2$][ClO$_4$]$_2$ and is related in structure to mixed-neutral-ligand species involving dmso[8] and dma (dimethylacetamide).[9] The dimer in the simple perchlorate (Figure 2) is centrosymmetric, with the (nine-) coordination geometry of the Ba atoms rendered somewhat irregular by the fact that four of the dmso-*O* donor atoms are bridging and one of the terminal sites on each Ba atom is occupied by unsymmetrically bidentate perchlorate [Ba−O 2.917(3), 3.056(3) Å]. If the perchlorate ligand is regarded as occupying a single coordination site, however, the geometry around the Ba metal centre is close to square antiprismatic. The perchlorate entities not found in the metal ion's primary coordination sphere appear to be involved in CH···O interactions with the dmso methyl groups (C···O approx. 3.3 Å), a mode of association which could presumably persist in solution. All the dmso molecules are coordinated and all by way of oxygen.

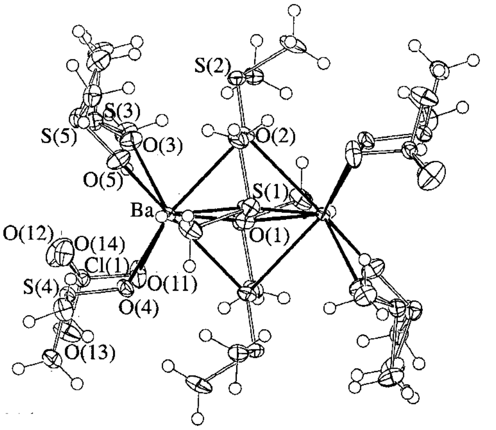

Figure 2. Projection of the centrosymmetric dinuclear cation [(dmso-*O*)$_3$(O$_2$Cl*O*$_2$)Ba(μ-dmso-*O*)$_2$]$_2$$^{4+}$; Ba−O(ClO$_4$) are 2.917(3), 3.055(3); Ba−O(dmso) 2.663(3)−2.710(2), Ba-(μ-dmso-*O*) 2.797(3), 2.827(2) Å; Ba···Ba is 3.9406(4) Å; only partial atom labelling is shown for clarity

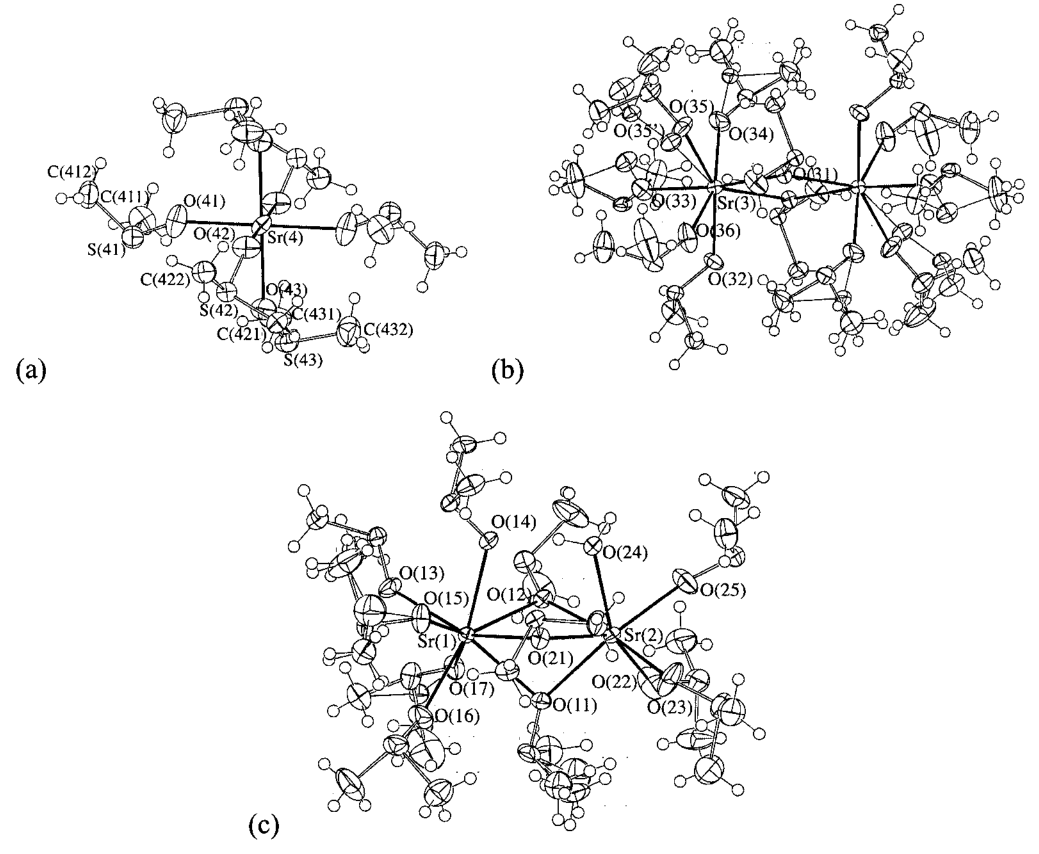

Figure 3. Projections of the cationic species in Sr$_7$(ClO$_4$)$_{14}$·40dmso·2H$_2$O; (a) the centrosymmetric [Sr(dmso-*O*)$_6$]$^{2+}$ cation, the maximum angular excursion from orthogonality being 91.6(2)°; Sr(4)−O(41,42,43) are 2.418(4), 2.452(5), 2.463(4) Å, corresponding Sr−O−S angles being 150.9(3), 133.0(2), 142.7(3)°; (b) the centrosymmetric [(dmso-*O*)$_5$Sr(μ-dmso-*O*)$_2$Sr(dmso-*O*)$_5$]$_2$$^{4+}$ cation; Sr(3)−O(31,31′) are 2.548(3), 2.692(4), while Sr−O(unidentate dmso) range between 2.473(10) and 2.524(3) Å; (c) the [(dmso-*O*)$_5$Sr(μ-dmso-*O*)$_3$-Sr(OH$_2$)(dmso-*O*)$_3$]$_2$$^{4+}$ cation; Sr(2)−O(11,12,21) are 2.582(4), 2.490(3), 2.584(3) Å; Sr(1)−O(11,12,21) 2.659(3), 2.634(4), 2.623(3) Å, with Sr−O−Sr 94.2(1), 97.04(9), 95.01(9)°, and O(11)···O(12, 21), O(12)···O(21) 2.864(5), 2.724(5), 3.326(4) Å; Sr−O(unidentate) about Sr(2) are 2.451(4)−2.491(5) (dmso), 2.636(4) (OH$_2$) and about Sr(1) 2.507(5)−2.641(4) Å

The complete coordination of dmso as an *O*-bound species is perhaps the only obvious common characteristic of both the Ba and Sr compounds. The structure determined for the Sr compound (Figure 3) shows that dmso is not the only solvent present and that the formula $Sr(ClO_4)_2·6dmso$ is imprecise, a better representation being $[Sr_7(dmso)_{40}(OH_2)_2][ClO_4]_{14}$ or, better still, [(dmso-*O*)$_5$Sr(μ-dmso-*O*)$_3$Sr(OH$_2$)(dmso-O)$_3$]$_2$[{(dmso-*O*)$_5$Sr(μ-dmso-O)}$_2$][Sr(dmso-O)$_6$][ClO$_4$]$_{14}$. The presence of a water ligand may simply reflect the use of solvents which were not completely dried and may mean that different species could be obtained under different crystallisation conditions, but the particular phase presently obtained is nonetheless of interest, even if it only exemplifies possible structures. (It may also be noted that in some related systems,[8] only certain mixed solvent species are readily crystallised.) Extraordinarily, the lattice contains three distinct strontium-containing species, two of them dinuclear, in which none of them is perchlorate coordinated. Sr^{II} is found in five different coordination environments: close to regular octahedral six-coordination in the mononuclear [Sr(dmso-O)$_6$]$^{2+}$; irregular seven-coordination, as [(*O*-dmso)$_5$Sr(μ-*O*-dmso)$_{(2/2)}$], in the centrosymmetric dinuclear species, as well as in the partially aquated moiety of the unsymmetrical dinuclear species [(dmso-*O*)$_3$(H$_2$O)Sr(μ-dmso-*O*)$_3$]; and irregular eight-coordination in the "homoleptic" component of the latter, [(dmso-*O*)$_5$Sr(μ-dmso-*O*)$_3$]. The bridging units of the dinuclear arrays contain fewer (three and two) μ-dmso-*O* units than that of the above dinuclear barium species, where there are four. The mononuclear species [Figure 3(a)] is a very rare example of a homoleptic, six-coordinate Sr^{II} complex with neutral ligands, the homoleptic aqua complex, for example, being a $[Sr(OH_2)_8]^{2+}$ species.[10] There is considerable divergence in the Sr−O−S angles, but only a loose correlation between those values and their associated Sr−O distances. In the centrosymmetric dinuclear cation, [Figure 3(b)], the two Sr−O distances of the obligate planar central four-membered ring are similar and longer than the closely ranged unidentate donor distances. The stereochemistry is irregular; there is one outstandingly large angle [O(31)−Sr(3)−O(33) 171.3(1)°], but the remaining five donor atoms do not constitute an acceptable equatorial plane. All Sr−O distances are longer than those found in the six-coordinate array. Three of the unidentate dmso moieties in this array are affected by disorder; in two, this is resolvable only in the sulfur atom, distributed over positions corresponding to inversion, but in dmso (35) it is more widespread, affecting the coordinating oxygen. In the unsymmetrical aquated dinuclear cation, there are now three μ-dmso-*O* moieties, of an irregular disposition most obvious in the variation of their O···O distances, Sr−O for the eight-coordinate Sr^{I} being longer than those to the seven-coordinate Sr^{II} metal centre; the unidentate dmso-O−Sr distances follow a similar pattern, with Sr(2)−O(24) (OH$_2$) longer than Sr(2)−O(22,23,25).

Within the group of alkaline earth elements, the coordination chemistry of Sr^{II} generally shows closer similarities to that of Ca^{II} than Ba^{II}.[5,11] Thus, the detection of several species within crystalline solvated $Sr(ClO_4)_2$ salt can be seen as being consistent with the extensive evidence for the coexistence of various solvated forms of Ca^{II},[12] though a comparison in the particular case of dmso solvates cannot yet be made [except that the elemental analysis indicates the Ca^{II} solvate to have the composition $Ca(ClO_4)_2·6dmso$]. The higher coordination number (9) presently observed for Ba^{II} than the mean for Sr^{II} is associated with bidentate coordination of perchlorate, consistent with a rather general tendency for oxyanion coordination, especially through unsymmetrical chelation, to be prominent with very heavy metals.[13] Possibly significantly, however, is the eight-coordination for Sr^{II}, accompanied by anion coordination, is seen in solid [Sr(dmso-*O*)$_2$(CF$_3$SO$_3$)$_2$].[14] The exploration of such subtleties by structural work can therefore be seen as providing an important contribution to the development of more sophisticated molecular models for electrolyte solutions. Following the suggestion of a referee, we note that one particular use of single-crystal data is to provide a coordination number associated with a given mean metal−donor atom distance, since solution X-ray measurements (LAXS, XAFS, EXAFS) frequently provide precise values for the latter but imprecise values for the former.[10b,12,14] Mean values for Sr−O (unidentate dmso) obtained from the present structures for six-, seven- and eight-coordination are 2.45(2), 2.50(2) and 2.56(3) Å, respectively, the value for seven-coordination being slightly less than that determined for $[Sr(dmso)_7]^{2+}$ in solution, although neither of the presently observed species containing seven-coordinate Sr is mononuclear.

Experimental Section

Synthesis and Crystal Growth

$Be(ClO_4)_2·4dmso$: Attempts to grow diffraction quality crystals of this known compound were unsuccessful.

$Mg(ClO_4)_2·6dmso$: Anhydrous $Mg(ClO_4)_2$ (1.0 g) was dissolved in ethanol (25 mL), dimethyl sulfoxide (5 mL) was added, followed by diethyl ether (25 mL) and the mixture was allowed to stand for 10 min as colourless crystals (1.90 g, 60 %) were deposited on the sides of the flask. These were recrystallised using the mixture of solvents, dmso/ethanol/diethyl ether, before crystals suitable for structural work were obtained by vapour diffusion of diethyl ether into a solution in dmso/ethanol (1:2). $C_{12}H_{36}Cl_2MgO_{14}S_6$ (692.0): calcd. C 20.83, H 5.24, S 27.80; found C 20.4, H 5.0, S (28.2).

"$Sr(ClO_4)_2·6dmso$": Concentrated perchloric acid (72 %) was added drop by drop to $SrCO_3$ (0.50 g) until most of the solid had dissolved. The mixture was transferred to a steam bath and heated. Acid addition was continued until a clear viscous solution had formed. This was heated for a further 2 min to ensure complete evolution of CO_2, then cooled to room temperature and dissolved in ethanol (40 mL). Dimethyl sulfoxide (10 mL) was added to this solution, followed by diethyl ether (50 mL). The mixture was cooled on ice to give a white, crystalline deposit (1.9 g, 75 %), which was then recrystallised twice from dmso/ethanol/diethyl ether. For elemental analysis, portion was dried by vacuum desiccation over silica gel. $C_{12}H_{36}Cl_2O_{14}S_6Sr$ (757.9): calcd. C 19.08, H 4.80, S 25.47; found C 18.9, H 4.4, S 25.1. $[Sr_7(ClO_4)_{14}·40dmso·H_2O$;

calcd. C 18.66, H 4.74, S 24.91.] Crystals suitable for structure determination were obtained by vapour diffusion of diethyl ether into a solution of the recrystallised material in dmso/ethanol (1:2).

(The Ca analogue was prepared in the same way from $\mathrm{CaCO_3}$. $\mathrm{Ca(ClO_4)_2\cdot 6dmso = C_{12}H_{36}CaCl_2O_{14}S_6}$ (708.1): calcd. C 20.4, H 5.15, Cl 10.0, S 27.2; found C 20.1, H 4.95, Cl 10.2, S 27.0. Large crystals of the complex could be obtained as for the Sr complex but they proved too fragile and too unstable for diffraction measurements to be possible.)

$\mathrm{Ba(ClO_4)_2\cdot 5dmso}$: $\mathrm{Ba(ClO_4)_2\cdot 3H_2O}$ was dissolved in dmso, ethanol and diethyl ether were added to give a white precipitate in quantitative yield. This was then twice recrystallised from dmso by addition of ethanol and diethyl ether. For analysis, the compound was dried by vacuum desiccation over silica gel. $\mathrm{C_{10}H_{30}BaCl_2O_{13}S_5}$ (726.99): C 16.5, H 4.16, Cl 9.75; found C 16.9, H 4.22, Cl 10.0.

Structure Determinations (T ca. 153 K; monochromatic Mo-K_α radiation, $\lambda = 0.71073$ Å; Bruker AXS CCD instrument).

$\mathrm{Mg(ClO_4)_2\cdot 6dmso}$, $\mathrm{[Mg(dmso\text{-}\mathit{O})_6[ClO_4]_2}$: $\mathrm{C_{12}H_{36}Cl_2MgO_{14}S_6}$ (692.0). Triclinic, $P\bar{1}$, $Z = 1$, $a = 7.6918(5)$, $b = 10.6220(7)$, $c = 10.6308(7)$ Å, $\alpha = 61.082(1)$, $\beta = 83.724(2)$, $\gamma = 84.696(2)°$, $V = 754.9$ Å^3. $D_c = 1.522\ \mathrm{g\cdot cm^{-3}}$. $R = 0.037$, $R_w = 0.042$ for $N_o = 7706$ reflections $[F > 4\sigma(F)]$ $(\theta_{max} = 60°)$.

"$\mathrm{Ba(ClO_4)_2\cdot 5dmso}$", $\mathrm{[(dmso\text{-}\mathit{O})_3(O_2Cl\mathit{O}_2)Ba(\mu\text{-}dmso\text{-}\mathit{O})_2]_2\text{-}[ClO_4]_2}$: $\mathrm{C_{20}H_{60}Ba_2Cl_4O_{26}S_{10}}$ (1453.8). Monoclinic, $P2_1/c$, $Z = 2$ dinuclear f.u., $a = 12.046(1)$, $b = 20.560(2)$, $c = 11.5985(9)$ Å, $\beta = 110.140(2)°$, $V = 2697$ Å^3. $D_c = 1.790\ \mathrm{g\cdot cm^{-3}}$. $R = 0.031$, $R_w = 0.040$ for $N_o = 6020$ $(\theta_{max} = 60°)$. All anion and solvent species were fully ordered in the refinement, as was also true of the Mg adduct.

$\mathrm{Sr_7(ClO_4)_{14}\cdot 40dmso\cdot 2H_2O \equiv [(dmso\text{-}\mathit{O})_5Sr(\mu\text{-}dmso\text{-}\mathit{O})_3Sr(OH_2)\text{-}(dmso\text{-}O)_3]_2[\{(dmso\text{-}\mathit{O})_5Sr(\mu\text{-}dmso\text{-}\mathit{O})\}_2][Sr(dmso\text{-}\mathit{O})_6][ClO_4]_{14}}$: $\mathrm{C_{80}H_{242}Cl_{14}O_{97}S_{40}Sr_7}$ (5167). Triclinic, $P\bar{1}$, $Z = 1$ f.u., $a = 13.1158(6)$, $b = 19.651(1)$, $c = 23.224(1)$ Å, $\alpha = 67.478(1)$, $\beta = 75.279(1)$, $\gamma = 89.144(1)°$, $V = 5339$ Å^3. $D_c = 1.607\ \mathrm{g\cdot cm^{-3}}$. $R_1 = 0.057$, $wR_2 = 0.072$ for No = 20926 (2θmax = 60°). Various anion and solvent components were modelled as disordered over pairs of sites, disordered fragment site occupancies refining to x, $1-x$ (minor components with isotropic displacement parameter forms), much seemingly concerted; thus for C(111, 112); S(15); S(172), C(172); S(34); O(60n); O(702−4), $x = 0.727(1)$, while for S(dmso 35); O(50n); $x = 0.5$. This affects the coordination sphere of Sr(3) where O(35)···O(35′) is 0.62(1) Å.

In the figures, non-hydrogen atoms are shown with 50 % probability amplitude displacement ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å. CCDC-14741, -214742 and -214743 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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