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The formation and collisionally activated dissociation of gas-phase singly and doubly charged Mg/DMSO complexes

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Abstract

DMSO complexes of Mg^{2+}, $[Mg(DMSO)_n]^{2+}$, have been created in the gas phase by electrospray ionization and have been interrogated by collisional activation. For $n > 4$, ions shed DMSO ligands only, but the low energy reactions for $n = 2$ are loss of first one and then a second methyl group with no loss of charge, giving $[Mg(DMSO)(CH_3SO)]^{2+}$ and $[Mg(CH_3SO)_2]^{2+}$. $[Mg(DMSO)_3]^{2+}$ loses DMSO preferentially but also competitively loses one methyl. $[Mg(DMSO)_4]^{2+}$ shows only a trace of methyl loss. Structures computed at the B3LYP/6-31G* level show that the metal–ligand bonding in $[Mg(DMSO)_2]^{2+}$ is mainly electrostatic with the geometry of the ligand only changed slightly by complexation. However, in $[Mg(DMSO)(CH_3SO)]^{2+}$ all atoms except the hydrogens are coplanar. Natural population analysis (NPA) shows that the DMSO sulfur has a significantly lower associated positive charge than it has in any other complex. $[MgO(DMSO)(CH_3SO)]^+$ ions may be observed in the electrospray spectrum at high cone potential. These ions show a unique breakdown pattern involving first the loss of SO_2 and then competitive formation of $MgCH_3{}^+$ and $[Mg (DMSO)]^+$. (Int J Mass Spectrom 216 (2002) 219–238) © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrospray ionization (ESI) is now the way of introducing multiply-charged metal ions into the gas phase from solution for mass spectrometric interrogation [1–13]. The metal ions are produced from salts in aqueous solution or in mixed water/organic solvent systems. The multiply-charged metal ions enter the gas phase associated with ligands from the solvent or from other molecules added to the solution. For example ions $[M(H_2O)_n]^{2+}$ have been produced from solutions of alkaline earth and doubly charged transition metal ions [1,14]. The addition to the solution of potential ligands such as dimethyl sulfoxide, pyridine and dimethylformamide leads to the incorporation of these molecules into the solvation shell. Such organic ligands generally form more stable first solvation shells for multiply charged metal cations than does water since they are in general less susceptible than is water to charge reduction via electron transfer from ligand to metal, followed by inter-ligand proton transfer and loss of the protonated

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ligand (Eq. (1)).

$$[M(H_2O)_n]^{2+} \rightarrow [MOH(H_2O)_{n-2}]^{+} + H_3O^{+} \qquad (1)$$

For example, although no triply-charged hydrated ions, $[M(H_2O)_n]^{3+}$ have been prepared by ESI, ions such as $[M(DMSO)_n]^{3+}$ (M = La, Ce, Nd, Sm) are stable and readily formed from salt solutions containing 10^{-3}–10^{-2} M DMSO [4]. Its significant polarizability, high dipole moment and lack of acidic hydrogens renders DMSO an ideal ligand for charge stabilization and hence for the formation by ESI of ligated, multiply charged metal cations.

The ease with which multiply-charged metal ions solvated by DMSO are produced by ESI is not consistent with the observation by Stace and coworkers that they could not produce $[Mg(DMSO)_n]^{2+}$ using their pick-up technique which has in the past been successful in producing many solvated multiply-charged metal cations [15–20]. The method involves electron impact ionization of a beam of argon/DMSO clusters containing metal atoms. As the authors state, there may be a flaw in their technique for the formation of the ions which prevents their observation since all the characteristics of the ligand are favorable for complex formation [19]. In this paper we report that $[Mg(DMSO)_n]^{2+}$ ions are indeed stable gas-phase complexes which are readily produced by ESI. We have used the technique to study the formation of $[Mg(DMSO)_n]^{2+}$ and other doubly and singly charged magnesium complexes obtained by spraying aqueous solutions of DMSO and magnesium ions. Collisionally activated dissociation (CAD) experiments have been used to investigate the ready loss of methyl radicals from the lower complexes. Ab initio calculations have been used to determine the structures of some of the ions and their decomposition products.

2. Experimental

Electrospray spectra were obtained using a triple sector mass spectrometer (quadrupole/hexapole/quadrupole, Quattro, FISONS, UK) in the manner that has been described previously [11,21,22]. Aqueous solutions containing $MgSO_4$ (1×10^{-3} M) and DMSO (1×10^{-2} M) were infused using a syringe pump at a flow rate of 5 μL min^{-1}. The metal capillary, counter electrode and cone potentials were varied for each solution in order to obtain spectra containing the required types of ions. The capillary potential was ∼+2.5 kV and the counter electrode potential was ∼+100 V. The intensities of the ions of interest in either normal mass spectra or CAD spectra were optimized by adjusting the electric field in the intermediate pressure region of the source between the cone and the grounded skimmer. The temperature of the desolvation chamber, through which dry nitrogen flowed, was 80 °C.

CAD spectra were obtained using argon as the target gas at pressures in the collision cell of 1–4×10^{-4} Torr. The energy of the ions entering the collision cell was determined by any residual energy in the jet expansion from the cone to the skimmer plus that gained due to the difference in potential between the grounded skimmer and the collision cell. The latter was electrically floated in the range 0 to −40 V with respect to ground. Ion retardation studies, for which a positive potential was applied to the collision cell, showed that the nominal laboratory ion energy of 0 eV corresponds to an actual average energy in the range 1–2 eV for a doubly charged ion. This small correction will be ignored and the translational energies of the ions entering the collision cell, quoted as E_{Lab}, will be those calculated from the collision cell potential.

All calculations were carried out using the Gaussian 98 suite of programs [23]. The density-functional method was used at the B3LYP/6-31G* level for geometry optimization. To evaluate the electronic energies, single point calculations were performed at QCISD(T)/6-311G(d,p) on the B3LYP/6-31G* geometries. Binding energies of metal ion–ligand complexes were obtained from the differences between QCISD(T)/6-311G(d,p) electronic energies and B3LYP/6-31G* zero-point vibrational energies. This method has been used by Stener and Calligaris to study DMSO binding in Ru(II) complexes who found that the computed internal coordinates and dipole moment of DMSO were in good agreement with experimental results [24].

3. Results and discussion

3.1. The formation of DMSO/Mg^{2+} complexes

Doubly charged complexes containing magnesium and DMSO, $[Mg(DMSO)_n]^{2+}$, are readily formed by ESI using aqueous solutions 10^{-3} M in a $MgSO_4$ and 10^{-2} M in DMSO. The range of the value of n observed in the spectra depends on the cone potential. At the low cone potential of +10 V, as seen in Fig. 1(a), n ranges from 4 to 8, with greatest intensity for $n = 4$. The range extended to higher values of n at lower cone potentials. The tetracoordinated ion is a very stable species, as discussed later. At higher cone potentials, the most intense peaks of formula $[Mg(DMSO)_n]^{2+}$ shift to lower values of n. In Fig. 1(b), for a cone potential of +35 V the only significant magnesium peaks are those of $[Mg(DMSO)_3]^{2+}$, $[Mg(DMSO)_2]^{2+}$ and their hydrates. Stace and coworkers' failure to observe any complexes of Mg^{2+} and DMSO must therefore, be due to a failure of their pick-up technique, although it is not immediately apparent why they could observe

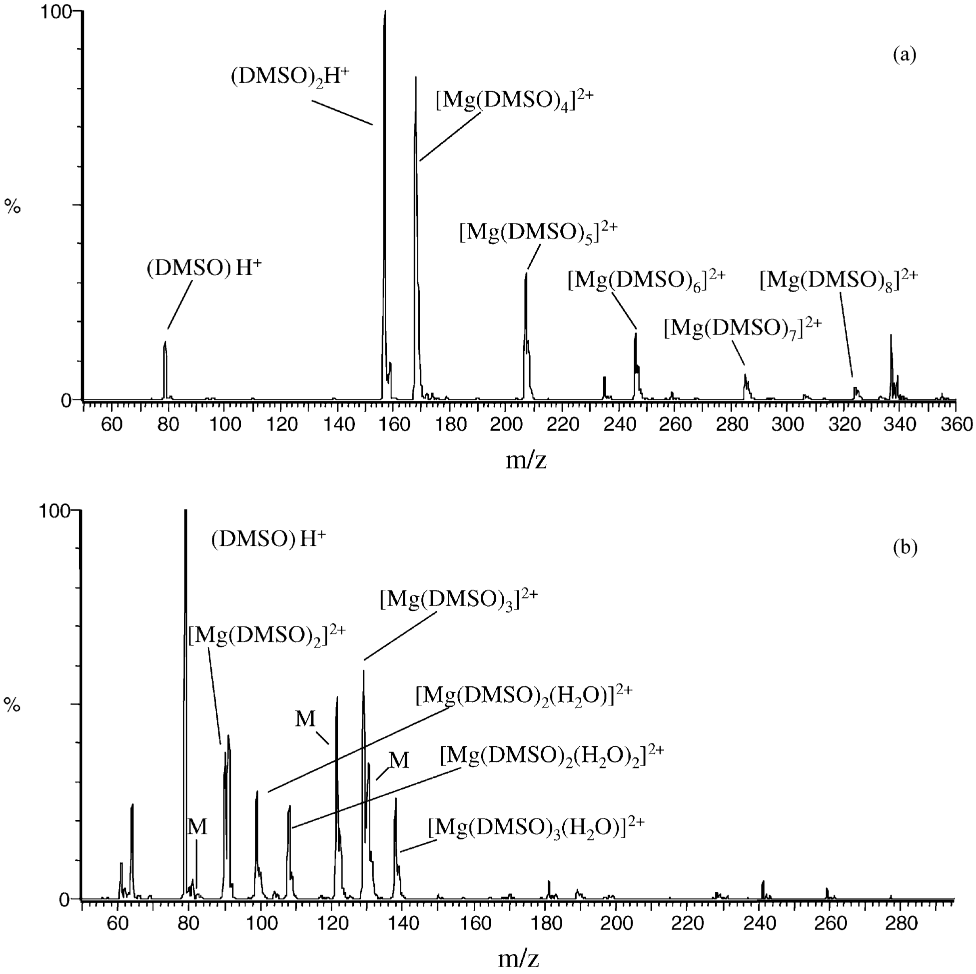

Fig. 1. The electrospray mass spectrum of an aqueous solution containing 1×10^{-3} M $MgSO_4$ and 1.0×10^{-2} M DMSO: (a) cone potential +10 V; (b) cone potential +35 V. The peaks marked M in (b) arise from the loss of a single methyl group from the adjacent $[Mg(DMSO)_n]^{2+}$ of higher m/z.

Mg^{2+} complexes containing dimethylformamide, acetone, etc. when none was observed for the equally strong ligand, DMSO [19].

With a cone potential of +35 V, protonated DMSO at *m*/*z* 79 is the base peak in the spectrum, but doubly charged magnesium-containing ions still constitute the major part of the total ion current. Some singly charged magnesium-containing ions are formed that are readily recognized by the isotopic patterns due to the combinations of the natural abundances of the isotopes of magnesium (^{24}Mg, 79%; ^{25}Mg, 11%; and ^{26}Mg, 10%) and sulfur (^{32}S, 95.0%; ^{33}S, 0.76% and ^{34}S, 4.22%). Singly charged ions are seen in Fig. 1(a) at *m*/*z* 235 and 337 and in Fig. 1(b) at *m*/*z* 181 and 241. The identities of most of these ions were not investigated but *m*/*z* 181 was of particular interest as discussed later. The presence of singly charged metal complexes is not unexpected since it is well known that increasing the ion translational energy in the cone-skimmer region leads to collisionally activated charge reduction.

In Fig. 1(b), $[Mg(DMSO)_n]^{2+}$ maximizes at $n = 3$, $[Mg(DMSO)_4]^{2+}$ is absent, and the only other prominent ion of this type is $[Mg(DMSO)_2]^{2+}$. The hydrates of both $[Mg(DMSO)_3]^{2+}$ and $[Mg(DMSO)_n]^{2+}$ are prominent in the spectrum, $[Mg(DMSO)_3]^{2+}$ being accompanied by $[Mg(DMSO)_3(H_2O)]^{2+}$ and $[Mg(DMSO)_2]^{2+}$ by both $[Mg(DMSO)_2(H_2O)]^{2+}$ and $[Mg(DMSO)_2(H_2O)_2]^{2+}$. $[Mg(DMSO)_3(H_2O)_3]^{2+}$, *m*/*z* 117, has a very small intensity, less than 1% base peak intensity, but there is not evidence for $[Mg(DMSO)_3(H_2O)_2]^{2+}$ at *m*/*z* 147. This pattern, together with the spectrum of Fig. 1(a), emphasizes the particular stability in the gas phase of Mg^{2+} when tetracoordinated. The preference for four ligands is also found for magnesium ions in the solid state and is not indicative of electronic saturation but is attributable to steric hindrance [25]. Doubly charged magnesium- containing ions other than $[Mg(DMSO)_n]^{2+}$ appear at the higher cone potentials when only the lower members ($n < 4$) of that series are prominent. Examples, marked M, can be seen in Fig. 1(b) at *m*/*z* 82.5, 121.5 and 130.5. When DMSO-d_6 rather than DMSO is present in the electrosprayed solution, *m*/*z* 82.5 increases by 4.5 units to *m*/*z* 87 and 121.5 increases by 7.5 units to *m*/*z* 129. *m*/*z* 130.5 also increases by 7.5 units to *m*/*z* 138. Since the ions are doubly charged, *m*/*z* 82.5 must contain three methyl groups and *m*/*z* 121.5 and 130.5 must each contain five methyl groups. *m*/*z* 82.5 is 7.5 units lower than *m*/*z* 90, i.e., it is equivalent in mass to *m*/*z* 90, $[Mg(DMSO)_2]^{2+}$, minus a methyl group and similarly *m*/*z* 121.5 is equivalent to an ion with one methyl group less than $[Mg(DMSO)_3]^{2+}$, *m*/*z* 129. *m*/*z* 130.5, 9 units higher than *m*/*z* 121.5 but containing the same number of methyl groups has a mass equivalent to that of *m*/*z* 121.5 plus one molecule of water. If these methyl losses occurred by CAD of $[Mg(DMSO)_n]^{2+}$ in the cone-skimmer region then such dissociations could be most readily studied using the collision cell, as described in the next section.

3.2. Collisionally activated dissociation of $[Mg(DMSO)_n]^{2+}$

The CAD spectra of $[Mg(DMSO)_n]^{2+}$ with large n ($n > 5$) and laboratory ion energies of 40 eV contained only peaks due to ions which had lost one or more DMSO ligands. Desolvation is the only reaction. This is consistent with studies of many doubly charged metal ion complexes which are found to have a critical value of n above which desolvation is the only collision induced reaction [14,19]. Even the triply charged $[La(DMSO)_6]^{3+}$ desolvates rather than entering into charge transfer reactions [4]. At 80 eV for $n = 4$, other types of ions appeared in the spectra, as illustrated in Fig. 2 for $[Mg(DMSO)_4]^{2+}$, $[Mg(DMSO)_3]^{2+}$ and $[Mg(DMSO)_2]^{2+}$. The spectra were obtained by using the relevant ions containing ^{24}Mg and ^{32}S. Ion identities were confirmed by collisionally dissociating other isotopomers, including those containing DMSO-d_6.

It is to be noted that at the fixed $E_{\mathrm{Lab}} = 80$ eV the center of mass energies associated with the collisions decrease in the order $[Mg(DMSO)_2]^{2+}$ (14.5 eV) > $[Mg(DMSO)_3]^{2+}$ (10.7 eV) > $[Mg(DMSO)_4]^{2+}$ (8.51 eV). This order is the reverse of the percentage decompositions as judged by the relative intensities of the parent ion to the sum of product ions in each of the three spectra of Fig. 2. The smaller the number of

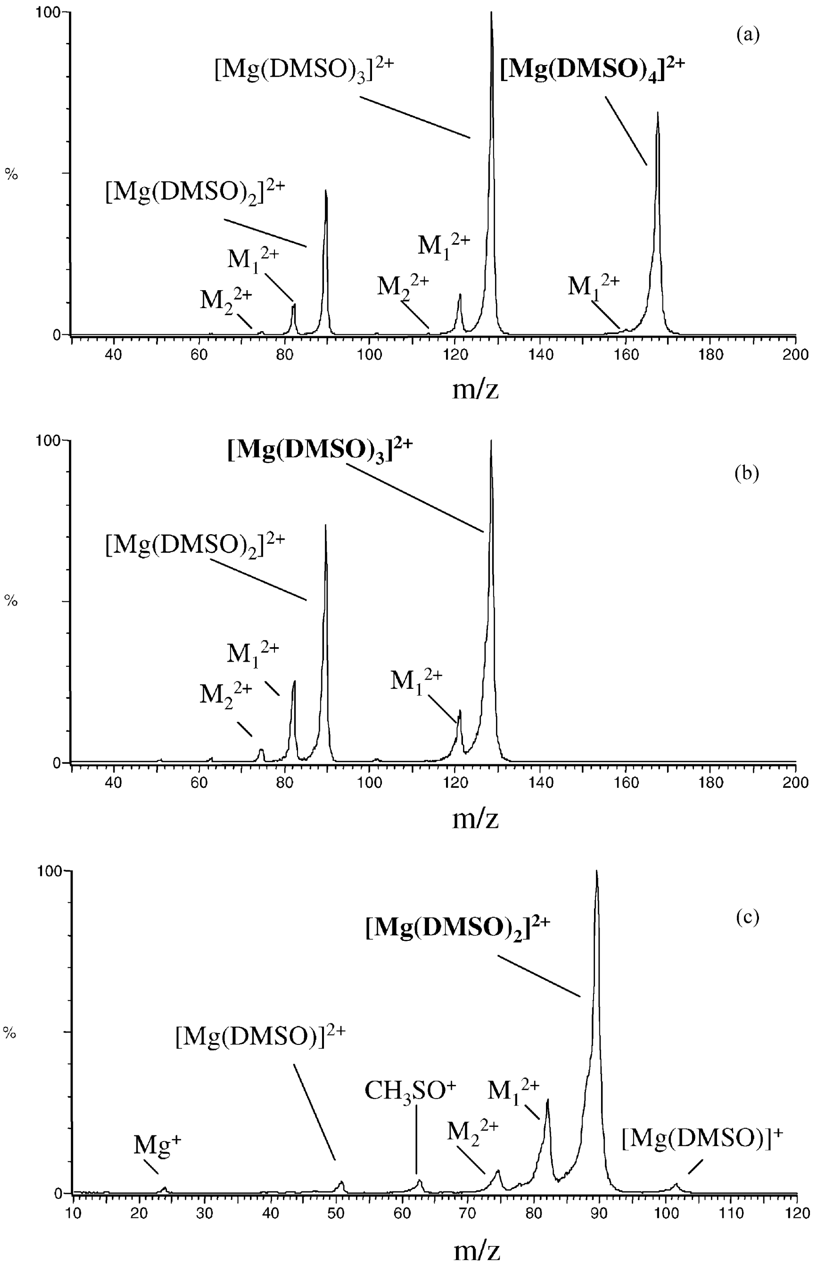

Fig. 2. The CAD spectra of (a) $[\mathrm{Mg(DMSO)_4}]^{2+}$; (b) $[\mathrm{Mg(DMSO)_3}]^{2+}$; and (c) $[\mathrm{Mg(DMSO)_2}]^{2+}$. $E_{\mathrm{Lab}} = 80\,\mathrm{eV}$; argon collision gas pressure 1×10^{-4} Torr. The peaks marked $\mathrm{M_1}$ and $\mathrm{M_2}$ are due to ions formed, respectively, by the loss of one and two methyl groups from the adjacent $[\mathrm{Mg(DMSO)}_n]^{2+}$. The parent ions are in bold and contain only ^{24}Mg and ^{32}S.

ligands, the more stable is the complex towards activated dissociation. This is not unexpected considering that in general the binding energy of a ligand in a complex decreases as the total number of ligands increases.

The major product ions in the CAD spectrum of $[\mathrm{Mg(DMSO)_4}]^{2+}$ are due to the loss of one and two ligands giving $[\mathrm{Mg(DMSO)_3}]^{2+}$ and $[\mathrm{Mg(DMSO)_2}]^{2+}$. At $E_{\mathrm{Lab}} = 80\,\mathrm{eV}$, $\mathrm{Mg(DMSO)_3}]^{2+}$ gives $[\mathrm{Mg(DMSO)_2}]^{2+}$ as the major product but $[\mathrm{Mg(DMSO)}]^{2+}$ is only a minor product in the spectrum of $[\mathrm{Mg(DMSO)_2}]^{2+}$. In the spectrum of $[\mathrm{Mg(DMSO)_4}]^{2+}$ there is an exceedingly small peak at *m*/*z* 160.5 which corresponds to an ion formed by loss of one methyl group from the parent ion. Each of $[\mathrm{Mg(DMSO)_3}]^{2+}$ and $[\mathrm{Mg(DMSO)_2}]^{2+}$ shows a much more prominent peak due to loss of one methyl and $[\mathrm{Mg(DMSO)_2}]^{2+}$ shows a peak at *m*/*z* 72.5 corresponding to the loss of two methyl groups. There is a trace of a peak at *m*/*z* 114 in the CAD spectrum of $[\mathrm{Mg(DMSO)_3}]^{2+}$ which is evidence for the loss of two methyl groups. Charge reduction by transfer of an electron from ligand to metal is demonstrated in the spectrum of $[\mathrm{Mg(DMSO)_2}]^{2+}$ by the presence of: $[\mathrm{Mg(DMSO)}]^{+}$ (*m*/*z* 102); a small peak due to DMSO^{+} at *m*/*z* 78; *m*/*z* 63 attributable to $\mathrm{CH_3SO}^{+}$, the base peak in the electron impact mass spectrum of DMSO; and Mg^{+}. The identifications of *m*/*z* 78 and 63 were confirmed by shifts to *m*/*z* 84 and 66 when DMSO-$\mathrm{d_6}$ was used. *m*/*z* 63, $[\mathrm{C,H_3,S,O}]^{+}$, has nine isomers whose structures have been investigated both theoretically and experimentally [26–31]. When *m*/*z* 63 is formed from the decomposition of ionized DMSO just above threshold, it has the structure $\mathrm{CH_2{=}SOH}^{+}$ whereas a few electron volts above the threshold, the structure is $\mathrm{CH_3SO}^{+}$ [26,27]. Electron transfer from DMSO (IE = 9.10 eV) to a bare Mg^{2+} (recombination energy = 15.03 eV) is highly exothermic and the same should be true of electron transfer in the Mg/DMSO complexes. *m*/*z* 63 if formed via DMSO^{+} is, therefore, probably $\mathrm{CH_3SO}^{+}$. However, it is possible that *m*/*z* 63 arises by loss of $[\mathrm{CH_3SO}]^{+}$ in an electron transfer reaction from $[\mathrm{Mg(DMSO)(CH_3SO)}]^{2+}$ or from $[\mathrm{Mg\,(CH_3SO)_2}]^{2+}$, both present in good yield at the higher collision energies.

The dependences on ion kinetic energy of the relative yields of major products at constant argon pressure in the CAD spectra of $[\mathrm{Mg(DMSO)_4}]^{2+}$ and $[\mathrm{Mg(DMSO)_2}]^{2+}$ are shown, respectively in Figs. 3 and 4. Peaks with intensities too low to be of significance were observed at high energies in the spectra of $[\mathrm{Mg(DMSO)_4}]^{2+}$ at: *m*/*z* 39 ($\mathrm{MgCH_3}^{+}$); *m*/*z* 51 ($[\mathrm{Mg(DMSO)}]^{2+}$); *m*/*z* 61 (possibly HCOS^{+}); *m*/*z* 63 ($\mathrm{CH_3SO}^{+}$); *m*/*z* 102 $[\mathrm{Mg(DMSO)}]^{+}$; *m*/*z* 114 $[\mathrm{Mg(CH_3SO)_2(DMSO)}]^{2+}$; and *m*/*z* 180 $[\mathrm{Mg(DMSO)_2}]^{+}$. Extremely minor products from $[\mathrm{Mg(DMSO)_2}]^{2+}$ not shown in Fig. 4 were at *m*/*z* 15 ($\mathrm{CH_3}^{+}$); *m*/*z* 39 ($\mathrm{MgCH_3}^{+}$); *m*/*z* 42.5 $[\mathrm{Mg(CH_3SO)}]^{2+}$; *m*/*z* 47 and 117. The latter two ions were not identified.

Fig. 3 shows that loss of first one and then a second DMSO ligand from $[\mathrm{Mg(DMSO)_4}]^{2+}$ occurs as the parent ion kinetic energy is increased. The simple loss of DMSO from product $[\mathrm{Mg(DMSO)_3}]^{2+}$ to give $[\mathrm{Mg(DMSO)_2}]^{2+}$ is in competition with loss of methyl giving $[\mathrm{Mg(DMSO)_2(CH_3SO)}]^{2+}$, both appearing at the same threshold energy of approximately 10 eV. The pathway for the further decomposition of $\mathrm{Mg(DMSO)_2}]^{2+}$ is delineated in the CAD spectrum of Fig. 4, loss of first one and then a second methyl group.

The loss of two methyl groups from the di-ligated $[\mathrm{Mg(DMSO)_2}]^{2+}$ was examined by studying the activated decomposition of $[\mathrm{Mg(DMSO)(DMSO\text{-}d_6)}]^{2+}$, *m*/*z* 93. This ion, in losing a methyl group, could form one or both of $[\mathrm{Mg(DMSO)(CD_3SO)}]^{2+}$ or $[\mathrm{Mg(CH_3SO)(DMSO\text{-}d_6)}]^{2+}$. Fig. 5 shows that both products are formed, the former appearing to be slightly favored. Loss of a second methyl group results in a single ion of *m*/*z* 76.5. This means that $\mathrm{CH_3}$ is lost from $[\mathrm{Mg(DMSO)(CD_3SO)}]^{2+}$ and $\mathrm{CD_3}$ is lost from $[\mathrm{Mg(CH_3SO)(DMSO\text{-}d_6)}]^{2+}$ giving the common product $[\mathrm{Mg(CH_3SO)(CD_3SO)}]^{2+}$.

$$\underset{m/z\,93}{[\mathrm{Mg(DMSO)(DMSO\text{-}d_6)}]^{2+}} \rightarrow [\mathrm{Mg(DMSO)(CD_3SO)}]^{2+} + \mathrm{CD_3} \quad (m/z\,84) \tag{2}$$

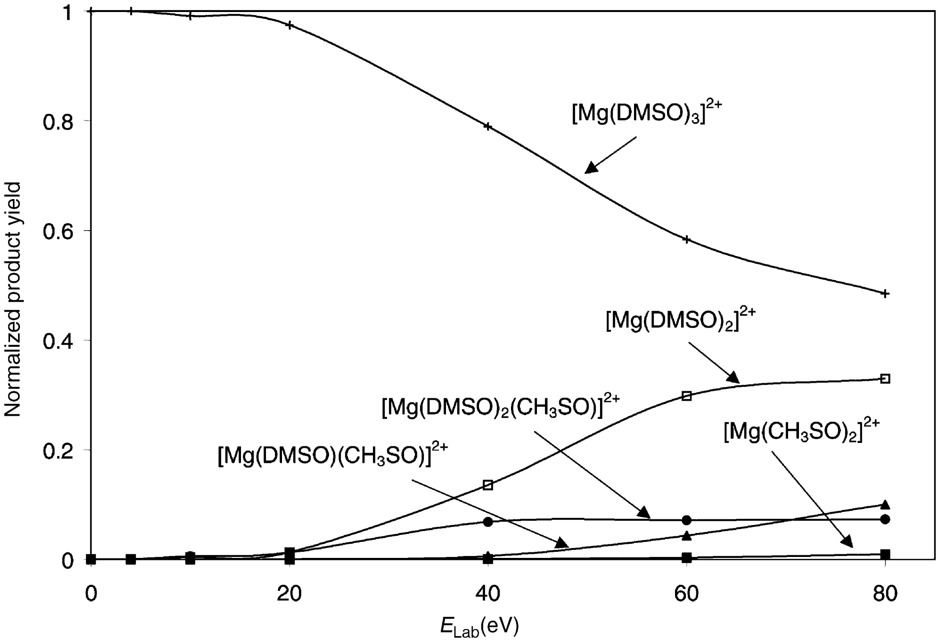

Fig. 3. The relative yields of product ions in the CAD spectrum of $[Mg(DMSO)_4]^{2+}$ as functions of laboratory ion energy. The products are derived from parent ions containing only ^{24}Mg and ^{32}S.

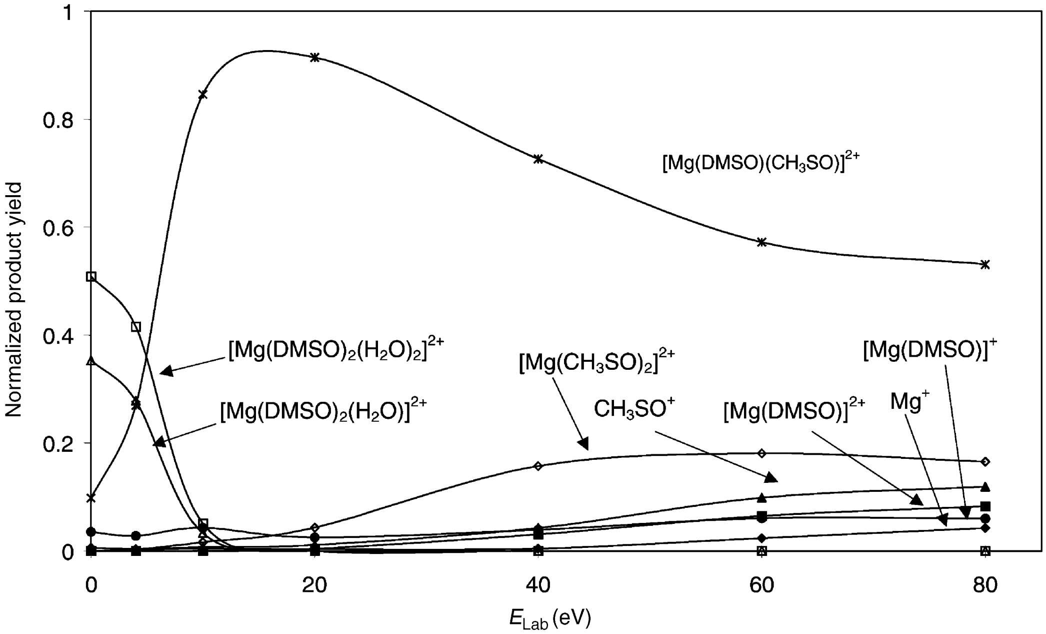

Fig. 4. The relative yields of product ions in the CAD spectrum of $[Mg(DMSO)_2]^{2+}$ as functions of laboratory ion energy. The products are derived from parent ions containing only ^{24}Mg and ^{32}S.

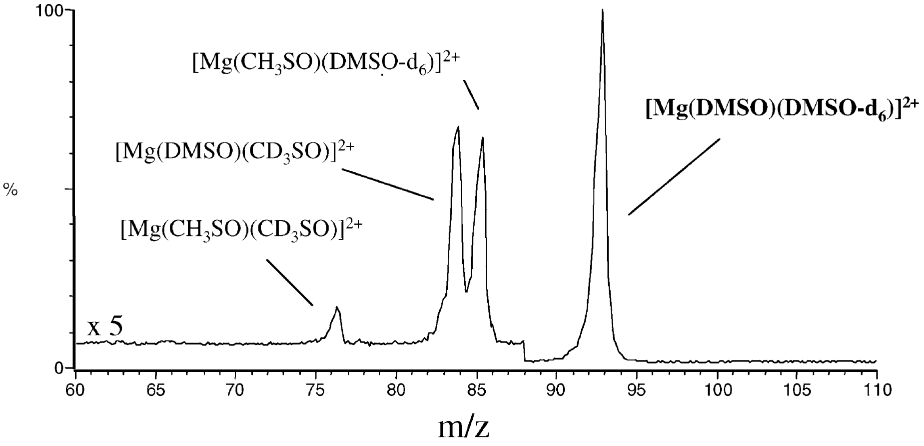

Fig. 5. The CAD spectrum of $[Mg(DMSO)(DMSO\text{-}d_6]^{2+}$ at a laboratory ion energy of 30 eV; argon collision gas pressure 1×10^{-4} Torr. The parent ion is in bold and contains only ^{24}Mg and ^{32}S.

$$\underset{m/z\,93}{[Mg(DMSO)(DMSO\text{-}d_6)]^{2+}} \rightarrow [Mg(CH_3SO)(DMSO\text{-}d_6)]^{2+} + CH_3 \quad (m/z\ 85.5) \tag{3}$$

$$\left.\begin{array}{l}[Mg(DMSO)(CD_3SO]^{2+} \\ [Mg(CH_3SO)(DMSO\text{-}d_6)]^{2+}\end{array}\right\} \rightarrow [Mg(CH_3SO)(CD_3SO)]^{2+} + C(H_3,D_3)\ (m/z\ 76.5) \tag{4}$$

The slightly greater yield of $[Mg(DMSO)(CD_3SO)]^{2+}$ than the product from the competing product channel, $[Mg(CH_3SO)(DMSO\text{-}d_6)]^{2+}$, indicates a slight preference for the loss of CD_3 over loss of CH_3. This preference was accentuated at low collision energies. It was surmised that this apparent isotope effect might be due to the presence at *m/z* 93 of an ion, $[Mg(DMSO)(CD_3SO)(H_2O)]^{2+}$ that is isobaric with $[Mg(DMSO)(DMSO\text{-}d_6)]^{2+}$. Loss of H_2O from $[Mg(DMSO)(CD_3SO)(H_2O)]^{2+}$ would also lead to *m/z* 84. Support for this idea was obtained from the CAD spectrum of $[Mg(DMSO)(CH_3SO)(H_2O)]^{2+}$, *m/z* 91.5, obtained in the absence of DMSO-d_6. Fig. 6 shows that at $E_{\text{Lab}} = 80$ eV, loss of H_2O is preferred over loss of either CH_3SO or DMSO. At very low collision energy only loss of water was observed. Preferential loss of H_2O over loss of any other ligand or group was also observed in the CAD of $[Mg(DMSO)_3(H_2O)]^{2+}$ and $[Mg(DMSO)(H_2O)_2]^{2+}$. In the case of all the above ions with water ligands, loss of H_2O occurred preferentially over loss of CH_3 at low collision energies. The "isotope effect" seen in Fig. 5 is therefore due to the presence of two isobaric ions at *m/z* 93.

Two other features of Fig. 6 are notable. The doubly charged ion $[Mg(DMSO)(H_2O)]^{2+}$ is present, albeit in low yield. A stripping reaction leading to loss of CH_3SO and retention of the much more weakly bound water ligand is possible at the higher energies. Also, $[Mg(DMSO)(CH_3SO)(H_2O)]^{2+}$ shows only a slight propensity for collisionally activated charge reduction at 40 eV collision energy. However, the presence of water leads to the formation of two singly charged ions, *m/z* 64 and 119, not previously observed. *m/z* 64 is probably protonated CH_3SO since *m/z* 119 would then be the complementary $[MgOH(DMSO)]^+$. One water and one CH_3SO in the same magnesium ion complex appear to participate in inter-ligand proton transfer (Eq. (5)), analogous to that described by Eq. (1).

$$[Mg(DMSO)(CH_3SO)(H_2O)]^{2+} \rightarrow [MgOH(DMSO)]^+ + CH_3SOH^+ \tag{5}$$

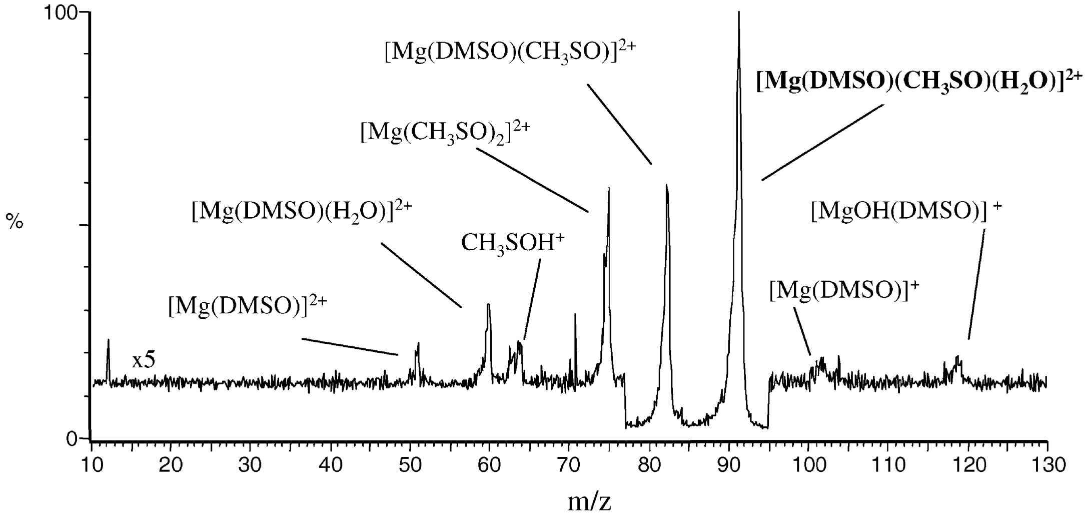

Fig. 6. The CAD spectrum of $[Mg(DMSO)(CH_3SO)(H_2O)]^{2+}$ at a laboratory ion energy of 80 eV; argon collision gas pressure 1×10^{-4} Torr. The parent ion is in bold and contains only ^{24}Mg and ^{32}S.

Turecek [30] has calculated at the MP2(FULL)/ 6-31 + G(d) level the enthalpy of formation (−33.9 kcal mol^{-1}), the O–H bond energy (68.7 kcal mol^{-1}) and the adiabatic ionization energy (8.71 eV) of methanesulfenic acid. The derived proton affinity of CH_3SO is then 234 kcal mol^{-1}. This is substantially greater than the proton affinity of DMSO (211 kcal mol^{-1} [32]) and production of ionized methanesulfenic acid rather than protonated DMSO is the preferred CAD reaction product of $[Mg(DMSO)(CH_3SO)(H_2O)]^{2+}$ brought about by inter-ligand proton transfer.

At very low ion energy, $[Mg(DMSO)_2]^{2+}$ adds one or two molecules of water in traversing the collision cell (Fig. 4). The addition of water is maximal at a nominal ion energy of 0 eV, as is expected for an association reaction occurring at low pressure, and is not observable at energies above 12 eV. The water is from the background of the instrument and from any present in the argon collision gas. The addition will be to ions with very low translational energies, both longitudinal and radial. We have shown previously that such ions are constrained by collision to travel along the axis of the hexapole collision cell where thermal association reactions can occur [33]. The addition of two water molecules is more prevalent than the addition of one water molecule by a factor of 1.5 at all energies. There was no evidence for the addition of a water molecule under similar conditions to $[Mg(DMSO)_4]^{2+}$. It was noted above that there was evidence in the ESI spectra at high cone potential for complexes of $[Mg(DMSO)_2]^{2+}$ containing three water molecules but no evidence for more than one water molecule attaching to $[Mg(DMSO)_3]^{2+}$. This observation is consistent with Mg^{2+} favoring tetracoordination. The presence of two water molecules in an inner shell will allow association with a third water molecule in an outer shell via two hydrogen bonds to the different water molecules. Association of a second water molecule in the outer solvation shell with the water molecule in $[Mg(DMSO)_3(H_2O)]^{2+}$ presumably leads to a weaker interaction and the non-appearance of this ion.

Since, as proved by the above CAD results, water is less strongly associated with Mg^{2+} than is DMSO, it is surprising to find more $[Mg(DMSO)_n(H_2O)_m]^{2+}$ ions in the ESI spectra obtained using an intermediate cone potential than when using a low cone potential (Fig. 1). The reason must be that the spectra are not representative of the states of the ions in the liquid phase, but are the result of gas-phase ion chemistry in the low-pressure cone-skimmer region. With a “high” electric field in this region, collisional desolvation is extensive and only the lower solvates predominate. Also, the time an ion spends in this region is relatively short and the opportunity for ligand exchange is relatively small. Water, being the major component of the infused solution, will feature strongly in the nascent ions and will remain so in the ions entering the spectrometer. At low cone potential, the ions are moving more slowly and have the opportunity of exchanging all their solvating water molecules for gas-phase DMSO molecules and also of retaining a larger solvation shell. The mass spectra at low cone potential are, therefore, dominated by $[\mathrm{Mg(DMSO)}_n]^{2+}$ ions, mixed solvent shells being absent.

Fig. 4 shows that loss of methyl from $[\mathrm{Mg(DMSO)_2}]^{2+}$ is the preferred decomposition path at all energies, accounting for more than 90% of the products at an ion energy of around 15 eV. Subsequent decomposition afforded by a higher energy input resulting from more energetic collisions leads to the loss of a second methyl group.

$$[\mathrm{Mg(DMSO)_2}]^{2+} \rightarrow [\mathrm{Mg(DMSO)(CH_3SO)}]^{2+} + \mathrm{CH_3} \qquad (6)$$

$$[\mathrm{Mg(DMSO)(CH_3SO)}]^{2+} \rightarrow [\mathrm{Mg(CH_3SO)_2}]^{2+} + \mathrm{CH_3} \qquad (7)$$

The only other doubly charged product ion in the CAD spectrum of $[\mathrm{Mg(DMSO)_2}]^{2+}$ is $[\mathrm{Mg(DMSO)}]^{2+}$ which appears only at the higher energies, and then increases in yield with increasing energy. Accompanying this ion are $[\mathrm{Mg(DMSO)}]^{+}$, Mg^{+} and $\mathrm{CH_3SO}^{+}$, formed by electron transfer from ligand to metal.

$$[\mathrm{Mg(CH_3SO)_2}]^{2+} \rightarrow [\mathrm{Mg(CH_3SO)}]^{+} + \mathrm{CH_3SO}^{+} \qquad (8)$$

$$[\mathrm{Mg(CH_3SO)}]^{+} \rightarrow \mathrm{Mg}^{+} + \mathrm{CH_3SO} \qquad (9)$$

One unexpected feature of the yield of the singly charged ions is that the yield of $[\mathrm{Mg(DMSO)}]^{+}$ (*m*/*z* 102) is small but not insignificant even at $E_{\mathrm{Lab}} = 0$ eV. The normalized yield is also almost invariant with temperature. No explanation for this observation is immediately apparent.

The paucity of charge reduction reactions in the CAD spectrum of $[\mathrm{Mg(CH_3SO)_2}]^{2+}$ is consistent with observations made regarding the collisionally activated decomposition reactions of the doubly charged alkaline earth metal cations complexes of another aprotic ligand, acetonitrile [10]. Ligand loss rather than charge reduction was observed.

3.3. Ab initio calculations of doubly charged DMSO/Mg^{2+} complexes

The computed minimum energy structures of DMSO, $[\mathrm{Mg(DMSO)}]^{2+}$ and $[\mathrm{Mg(DMSO)_2}]^{2+}$ are shown in Fig. 7 and those of $\mathrm{CH_3SO}$, $[\mathrm{Mg(CH_3SO)}]^{2+}$ and $[\mathrm{Mg(CH_3SO)(DMSO)}]^{2+}$ are in Fig. 8. The geometry of DMSO is almost identical with that obtained by Stener and Calligaris [24] and slightly overestimates the bond lengths compared with those from experiment [34,35]. The calculated dipole moment of 3.67 D is in good agreement with the experimental value of 3.9 D. Attachment of Mg^{2+} in both $[\mathrm{Mg(DMSO)}]^{2+}$ and $[\mathrm{Mg(DMSO)_2}]^{2+}$ is at oxygen, the favored site for hard Lewis acids such as Mg^{2+} [23,36]. The association of one DMSO with Mg^{2+} leads to an increase in the S–O bond length of 0.114 Å and an accompanying decrease in the C–S bond lengths of 0.027 Å. This effect of polarization is decreased in the individual ligands of $[\mathrm{Mg(DMSO)_2}]^{2+}$ where the increase in the S–O bond length is 0.085 Å and the decrease of the C–S bond length is 0.026 Å. These changes from the mono- to the di-ligated ions are accompanied by the increase in Mg–O bond length, from 1.806 Å in $[\mathrm{Mg(DMSO)}]^{2+}$ to 1.841 Å in $[\mathrm{Mg(DMSO)_2}]^{2+}$. Accompanying these changes in the geometry of DMSO upon association with Mg^{2+} are: increases in the CSC bond angles, 6° in $[\mathrm{Mg(DMSO)}]^{2+}$ and slightly less than 5.1°, in $[\mathrm{Mg(DMSO)_2}]^{2+}$; and significant decreases in the OSC angles, the arrangement of bonds around S in $[\mathrm{Mg(DMSO)}]^{2+}$ being almost trigonally symmetric and those in $[\mathrm{Mg(DMSO)_2}]^{2+}$ being slightly less so.

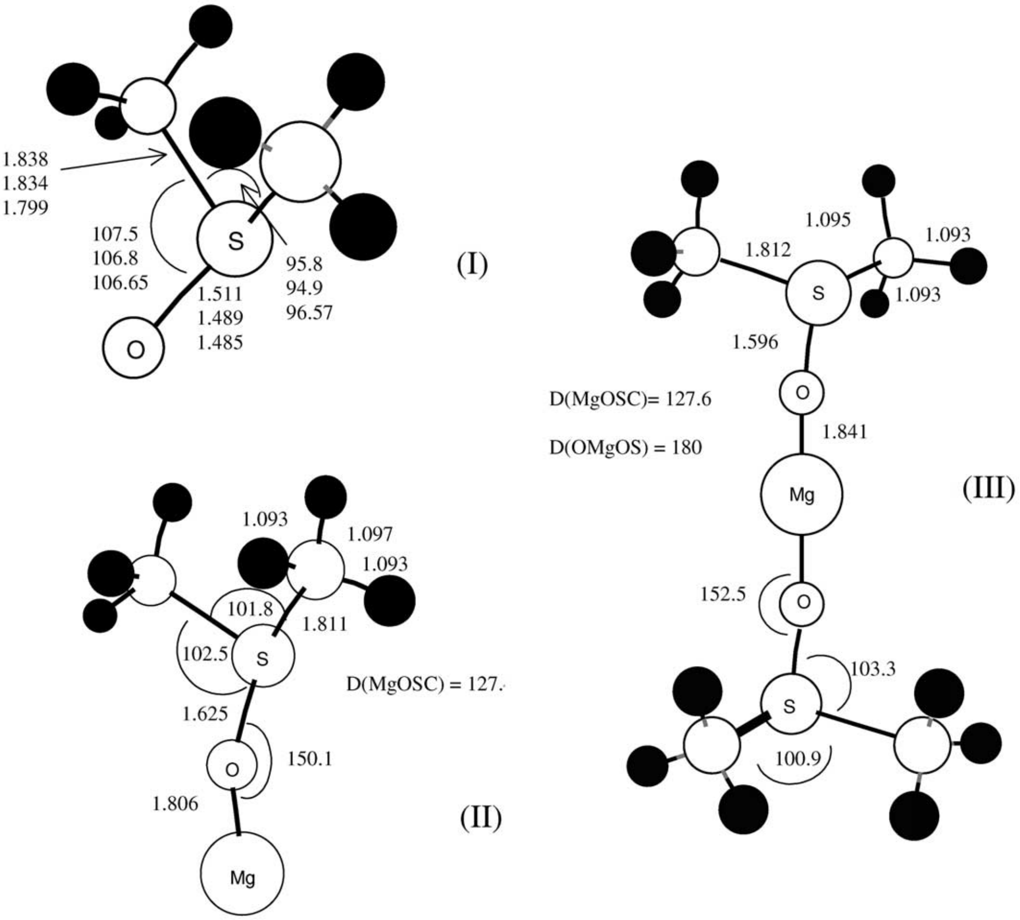

Fig. 7. The computed minimum energy structures of (I) DMSO; (II) $[Mg(DMSO)]^{2+}$; and (III) $[Mg(DMSO)_2]^{2+}$. Distances are in 8_3 and angles are in degrees. The data for I are, top to bottom: this work; [24]; experimental results, [34,35].

Although it is not immediately obvious from Fig. 7, $[Mg(DMSO)_2]^{2+}$ has C_{2h} symmetry, the atoms SOMgOS being coplanar and the MgOSC dihedral angles are 127.6°. The bonding around sulfur is, therefore, sp^3 in character.

Fig. 8 shows that the free radical CH_3SO has a longer, 0.023 Å, S–O bond than DMSO but the S–C length and OSC angles are very similar. The changes in these parameters when CH_3SO associates with Mg^{2+} are similar to those noted above for DMSO. The S–O bond length increases by 0.057 Å and the S–C bond decreases by 0.051 Å. The Mg–O bond length of 1.840 Å is larger than the 1.806 Å in $[Mg(DMSO)]^{2+}$ and the MgOSC dihedral angle is 180°. There is a remarkable change in the structure of the DMSO ligand to Mg^{2+} when the other ligand is CH_3SO rather than a second DMSO. $[Mg(DMSO)(CH_3SO)]^{2+}$ has C_s symmetry, all atoms except the hydrogens being coplanar. The Mg–$OS(CH_3)_2$ bond length of 1.810 Å is now only 0.004 Å longer than that in $[Mg(DMSO)]^{2+}$ and hence much shorter than the 1.841 Å in $[Mg(DMSO)_2]^{2+}$. The DMSO ligand in $[Mg(DMSO)(CH_3SO)]^{2+}$ has assumed planarity with the CSC angle slightly larger than the CSO angles. The character of the bonding of sulfur in the DMSO is now close to sp^2 rather than the sp^3 in $[Mg(DMSO)_2]^{2+}$ and $[Mg(DMSO)]^{2+}$.

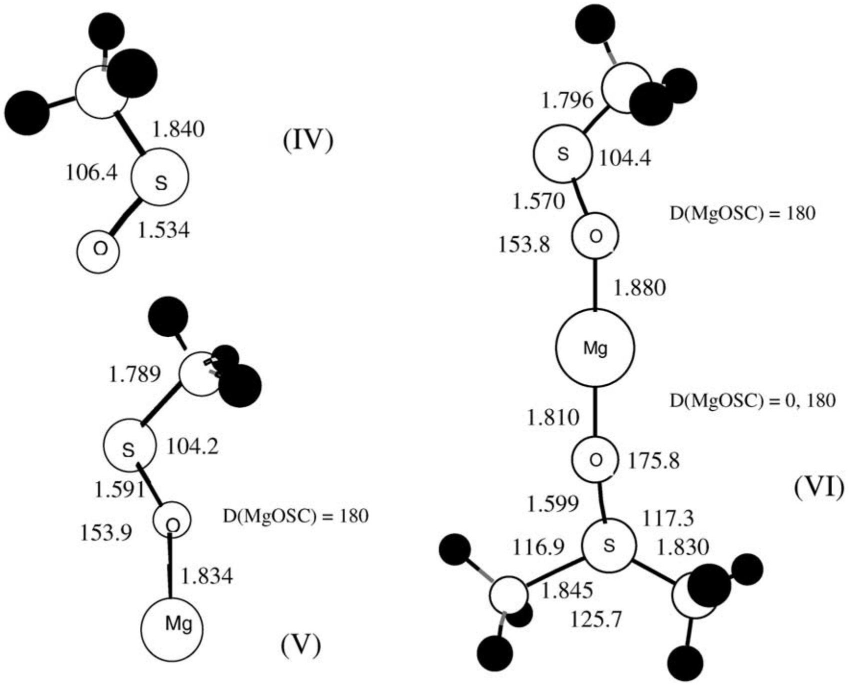

Fig. 8. The computed minimum energy structures of (IV) CH_3SO; (V) $[Mg(CH_3SO)]^{2+}$; and (VI) $[Mg(DMSO)(CH_3SO)]^{2+}$. Distances are in 8_3 and angles are in degrees.

A natural population analysis (NPA) was performed on all the structures in Figs. 7 and 8. This analysis gives a more realistic partitioning of the electrons to the constituent atoms than does a Mulliken population analysis and hence a better picture of the charge that can be associated with each atom [37,38]. The results, in Table 1, show that the amount of charge transfer from ligand to metal is small for all complexes but does increase with the number of ligands. The metal–ligand binding is, therefore, mainly electrostatic in nature, influenced by the large dipole moments of DMSO and CH_3SO, computed, respectively, as 3.67 and 2.96 D, and the large energy difference between the filled 2s and the vacant 3s and 3p levels of Mg^{2+}.

Table 1
Natural population analysis

	Mg	O	S	C
CH_3SO	–	−0.702	0.833	−0.896
DMSO	–	−0.958	1.261	−0.897
$[Mg(CH_3SO)]^{2+}$	1.91	−1.16	1.202	−0.91
$[Mg(DMSO)]^{2+}$	1.88	−1.25	1.29	−0.86
$[Mg(DMSO)_2]^{2+}$	1.83	−1.23	1.30	−0.87
$[Mg(DMSO)(CH_3SO)]^{2+}$	1.84	−1.21[a]	1.05[a]	−0.76[a]
		−1.10[b]	1.16[b]	−0.91[b]

[a] Atoms in DMSO ligand.
[b] Atoms in CH_3SO ligand.

Table 1 shows that the negative charge on oxygen increases substantially when one DMSO molecule associates with Mg^{2+} but the positive charge on sulfur increases to a much lesser extent. There is a much greater polarization of the O–S bond when CH_3SO associates with Mg^{2+}. The large increase of negative charge on O is accompanied by a substantial increase of positive charge on S. In $[Mg(DMSO)(CH_3SO)]^{2+}$ the positive charge on the S atom of the DMSO ligand is lower than in any other complex or in the neutral molecule. This reflects the sp^2 character of the binding at this atom and the presence of a lone pair of electrons in the $3p_z$ orbital.

Enthalpy changes were computed for the association of the first and second DMSO molecule with Mg^{2+}, Eqs. (10) and (11).

$$\mathrm{Mg^{2+} + DMSO \rightarrow [Mg(DMSO)]^{2+}} \quad \Delta H^\circ = -146\,\mathrm{kcal\,mol^{-1}} \tag{10}$$

$$\mathrm{[Mg(DMSO)]^{2+} + DMSO \rightarrow [Mg(DMSO)_2]^{2+}} \quad \Delta H^\circ = -115\,\mathrm{kcal\,mol^{-1}} \tag{11}$$

The enthalpy change of $-146\,\mathrm{kcal\,mol^{-1}}$ for the addition of one molecule is significantly more negative than the $-81.5\,\mathrm{kcal\,mol^{-1}}$ [39] and $-81.8\,\mathrm{kcal\,mol^{-1}}$ [38] calculated at B3LYP/6-311 + +G(d,p) for the addition of one molecule of water to Mg^{2+}. It is also larger than the $121.2\,\mathrm{kcal\,mol^{-1}}$ calculated at the same level for the association of one molecule of acetone with Mg^{2+} [38]. Although the present computations were carried out at a lower level of geometry optimization, a larger value for the association of Mg^{2+} with DMSO is to be expected because of the larger dipole moment and polarizability of DMSO (3.96 D, 7.93 Å^3) compared with those of both water (1.85 D, 1.48 Å^3) and acetone (2.86 D, 6.33 Å^3). There are no other data available for comparing the enthalpy change for the association of a bare, doubly charged metal cation with DMSO. The bond energy in the association of DMSO with $Ru(NH_3)_5{}^{2+}$ was computed as $200\,\mathrm{kcal\,mol^{-1}}$, a higher value than found for Mg^{2+} because of the opportunity for back bonding into the empty π^*(S–O) orbital by Ru^{2+} [23], a stabilizing effect that is not available to Mg^{2+}. The addition of DMSO to $[Mg(DMSO)]^{2+}$ is exothermic by $115\,\mathrm{kcal\,mol^{-1}}$, consistent with the accompanying increase in the length of the metal–oxygen bond.

The computed enthalpy change for the association of Mg^{2+} with CH_3SO is $23\,\mathrm{kcal\,mol^{-1}}$ less than for association with DMSO.

$$\mathrm{Mg^{2+} + CH_3SO \rightarrow [MgCH_3SO]^{2+}} \quad \Delta H^\circ = -123\,\mathrm{kcal\,mol^{-1}} \tag{12}$$

The addition of CH_3SO to $[Mg(DMSO)]^{2+}$ is $54\,\mathrm{kcal\,mol^{-1}}$ exothermic while the addition of DMSO to $[MgCH_3SO]^{2+}$ is $77\,\mathrm{kcal\,mol^{-1}}$ exothermic.

$$\mathrm{CH_3SO + [Mg(DMSO)]^{2+} \rightarrow [Mg(DMSO)(CH_3SO)]^{2+}} \quad \Delta H^\circ = -54\,\mathrm{kcal\,mol^{-1}} \tag{13}$$

$$\mathrm{DMSO + [Mg(CH_3SO)]^{2+} \rightarrow [Mg(DMSO)(CH_3SO)]^{2+}} \quad \Delta H^\circ = -77\,\mathrm{kcal\,mol^{-1}} \tag{14}$$

Elimination of methyl from $[Mg(DMSO)_2]^{2+}$ is calculated to be endothermic by $110\,\mathrm{kcal\,mol^{-1}}$.

$$\mathrm{[Mg(DMSO)_2]^{2+} \rightarrow [Mg(DMSO)(CH_3SO)]^{2+} + CH_3} \quad \Delta H^\circ = +110\,\mathrm{kcal\,mol^{-1}} \tag{15}$$

Loss of a second methyl leads to $[Mg(CH_3SO)_2]^{2+}$, that is Mg^{2+} associated with two radicals. This biradical product can be in either a singlet or a triplet state, the latter being lower in energy by $29\,\mathrm{kcal\,mol^{-1}}$.

$$\mathrm{[Mg(DMSO)(CH_3SO)]^{2+} \rightarrow [Mg(CH_3SO)_2]^{2+}(triplet) + CH_3} \quad \Delta H^\circ = 25\,\mathrm{kcal\,mol^{-1}} \tag{16}$$

The above data allow an understanding of the dependence on collision energy of the product yields in the CAD spectrum of $[Mg(DMSO)_2]^{2+}$. Elimination of methyl is in competition with loss of a complete DMSO. The former is slightly less endothermic, $110\,\mathrm{kcal\,mol^{-1}}$ vs. $115\,\mathrm{kcal\,mol^{-1}}$ and takes precedence. The possible decomposition reactions of the product, $[Mg(DMSO)(CH_3SO)]^{2+}$ are: loss of a methyl; loss of CH_3SO; and loss of DMSO. The respective reaction endothermicities are: 25, 54, and $77\,\mathrm{kcal\,mol^{-1}}$. Fig. 4 shows that the product yields are consistent with the calculated endothermicities, $[Mg(CH_3SO)_2]^{2+}$ is the major product, $[Mg(DMSO)]^{2+}$ is about half as intense and $[Mg(CH_3SO)]^{2+}$ is not observed. The barrier for methyl loss must be less than the enthalpy change for loss of a whole ligand, a process whose only barrier will be its endothermicity. It can be surmised, although no calculations were performed, that as *n* increases and the enthalpy of association of each succeeding DMSO in $[Mg(DMSO)_n]^{2+}$ becomes less negative, methyl loss becomes energetically less competitive than loss of a whole ligand. Hence loss of DMSO and not loss of methyl is the predominant reaction of $[Mg(DMSO)_3]^{2+}$.

As a check on the confidence to be placed in the computed reaction enthalpies, Eqs. (11), (13) and (15) may be used to obtain Eq. (17).

$$\mathrm{DMSO} \rightarrow \mathrm{CH_3SO}^{\bullet} + {}^{\bullet}\mathrm{CH_3} \quad \Delta H^{\circ} = +49\,\mathrm{kcal\,mol^{-1}} \tag{17}$$

This value for the enthalpy of dissociation of DMSO to the sulfinyl and methyl radicals is in good agreement with the range of 53–56 $\mathrm{kcal\,mol^{-1}}$ estimated by Benson [40] and Thorson [41].

If tetracoordination is the preferred state of Mg^{2+}, then methyl loss occurs significantly only when there is a vacant site on the metal. (There was an extremely small methyl loss from $[Mg(DMSO)_4]^{2+}$.) This suggests that metal insertion into the S–C bond followed directly by loss of methyl occurs. However, such a process would lead to a metal–sulfur bond while calculation shows that the bond is to the O of CH_3SO. It may be just the case that at $n = 3$ methyl loss becomes energetically competitive with loss of a whole ligand since, as previously mentioned, with few exceptions the binding energy of a ligand increases as the total number of ligands decreases.

4. Singly charged DMSO/magnesium complexes

The types of ions present in the ESI spectrum of the aqueous solution of any doubly charged metal ion are dependent on the value of the cone potential. If no other potential ligands are present in solution then the $[M(H_2O)_n]^{2+}$ ions present at low cone potential are subjected to dehydration (Eq. (18)) and charge reduction by collisional activation at higher cone potentials. The general charge reduction reaction is inter-ligand proton transfer Eq. (19). In Eq. (19) one or more of the uncomplexed water molecules may be associated with the hydronium ion.

$$[\mathrm{M(H_2O)}_n]^{2+} \rightarrow [\mathrm{M(H_2O)}_{n-x}]^{2+} + x\mathrm{H_2O} \tag{18}$$

$$[\mathrm{M(H_2O)}_n]^{2+} \rightarrow [\mathrm{MOH(H_2O)}_{n-x}]^{+} + \mathrm{H_3O}^{+} + (x-2)\mathrm{H_2O} \tag{19}$$

Mixed ligand complexes such as $[Mg(DMSO)_2(H_2O)]^{2+}$ and $[Mg(DMSO)_2(H_2O)_2]^{2+}$ were observed in abundance in spectra from aqueous solutions containing both Mg^{2+} and DMSO at cone potentials of +25 to +40 V. At lower potentials, doubly charged ions containing only DMSO predominated. When the cone potential was raised to +60 V and above, the spectrum contained both singly and doubly charged ions in roughly equal proportions. This is illustrated in Fig. 9(a) and (b) for solutions containing DMSO and DMSO-d_6, respectively. Only the major singly charged ions are identified in the spectra. The base peak in Fig. 9(a) is *m*/*z* 64, which shifts to *m*/*z* 67 in Fig. 9(b). These ions, CH_3SOH^+ and CD_3SOH^+, result from the decomposition of protonated DMSO and DMSO-d_6, respectively. CH_3S^+ (*m*/*z* 47) and CD_3S^+ (*m*/*z* 50) arise from the same source.

m/*z* 117 and 181 are the major Mg-containing, singly charged ions in Fig. 9(a) and these shift to, *m*/*z* 126 and 190 when DMSO-d_6 is used. Therefore, *m*/*z* 117 contains nine hydrogens, as does *m*/*z* 181. The same mass difference of 64 u for both pairs of peaks was intriguing and their identities were, therefore, investigated by CAD.

The CAD spectrum of *m*/*z* 117 at $E_{\mathrm{Lab}} = 20$ eV is shown in Fig. 10(a) while the CAD spectrum of its perdeuterated analogue, *m*/*z* 126, is in Fig. 10(b). The two major products from *m*/*z* 117 result from losses of 15 and 78 u, giving *m*/*z* 102 and 39, respectively. The analogous products from *m*/*z* 126 are *m*/*z* 108 and 42 i.e., losses of 18 and 84 u. In both spectra there is a small Mg^+ peak at *m*/*z* 24, which increases in intensity when the collision energy increases but is always negligibly small. At $E_{\mathrm{Lab}} = 40$ eV another new product appears at *m*/*z* 87 for the protiated and at *m*/*z* 90 for the perdeuterated DMSO systems. The

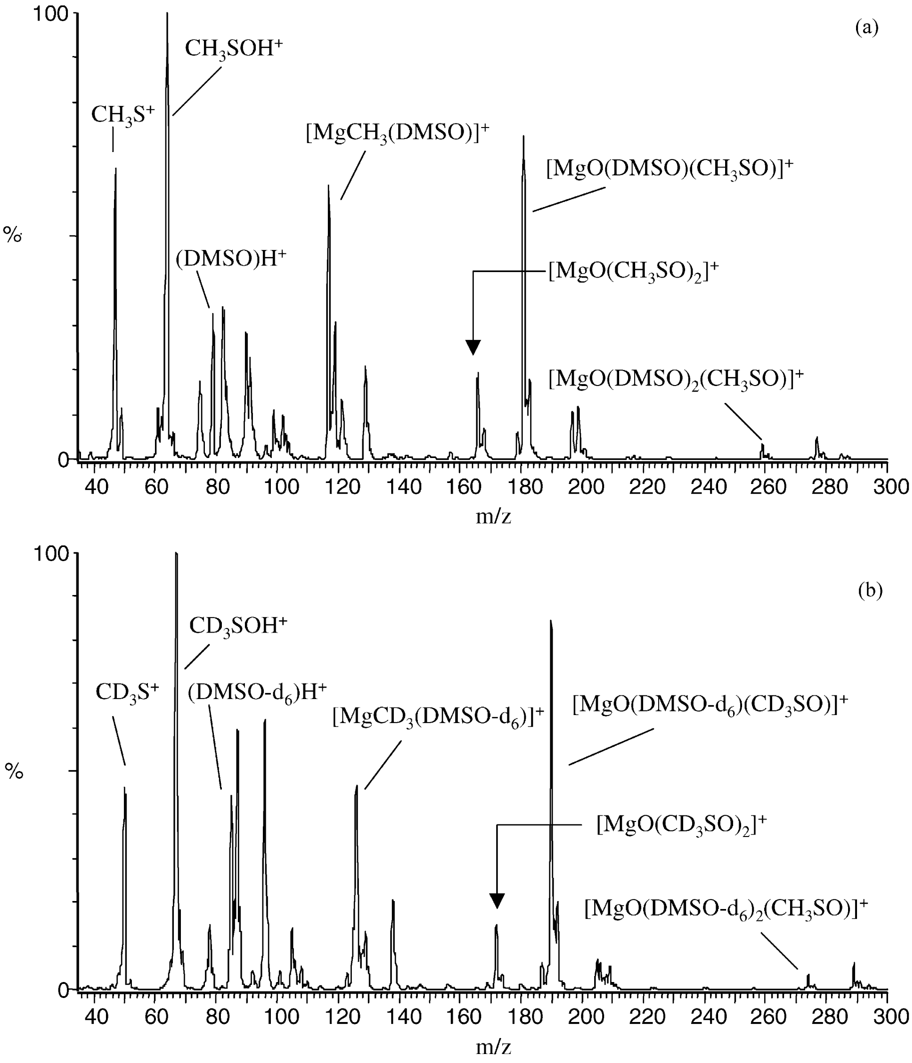

Fig. 9. ESI spectra obtained from (a) aqueous $MgSO_4$/DMSO solutions; and (b) aqueous $MgSO_4$/DMSO-d_6 solutions. Cone potential +60 V.

above observations are consistent with *m*/*z* 117 being $[MgCH_3(DMSO)]^+$ which decomposes according to the following scheme to give two major products.

$$\underset{m/z\,117}{[MgCH_3(DMSO)]^+} \rightarrow \underset{m/z\,102}{[Mg(DMSO)]^+} + CH_3 \qquad (20)$$

$$\underset{m/z\,117}{[MgCH_3(DMSO)]^+} \rightarrow \underset{m/z\,39}{MgCH_3{}^+} + DMSO \qquad (21)$$

m/*z* 102 could be the isobaric $[MgCH_3(CH_3SO)]^+$ rather than $[Mg(DMSO)]^+$ but this was ruled out by the use of a solution equimolar in DMSO and DMSO-d_6. The ESI spectrum contained not only *m*/*z* 117 and 126, but also *m*/*z* 120 and 123. The CAD spectrum of *m*/*z* 120 had major ions at *m*/*z* 42, $MgCD_3{}^+$, and 102, $[Mg(DMSO)]^+$, identifying it as $[MgCD_3(DMSO)]^+$. Similarly, the CAD spectrum of *m*/*z* 123 had major ions at *m*/*z* 39, $MgCH_3{}^+$, and 108, $[Mg(DMSO\text{-}d_6)]^+$, identifying it as $[MgCH_3(DMSO\text{-}d_6)]^+$. In each spectrum there was a small peak corresponding to the loss of a methyl

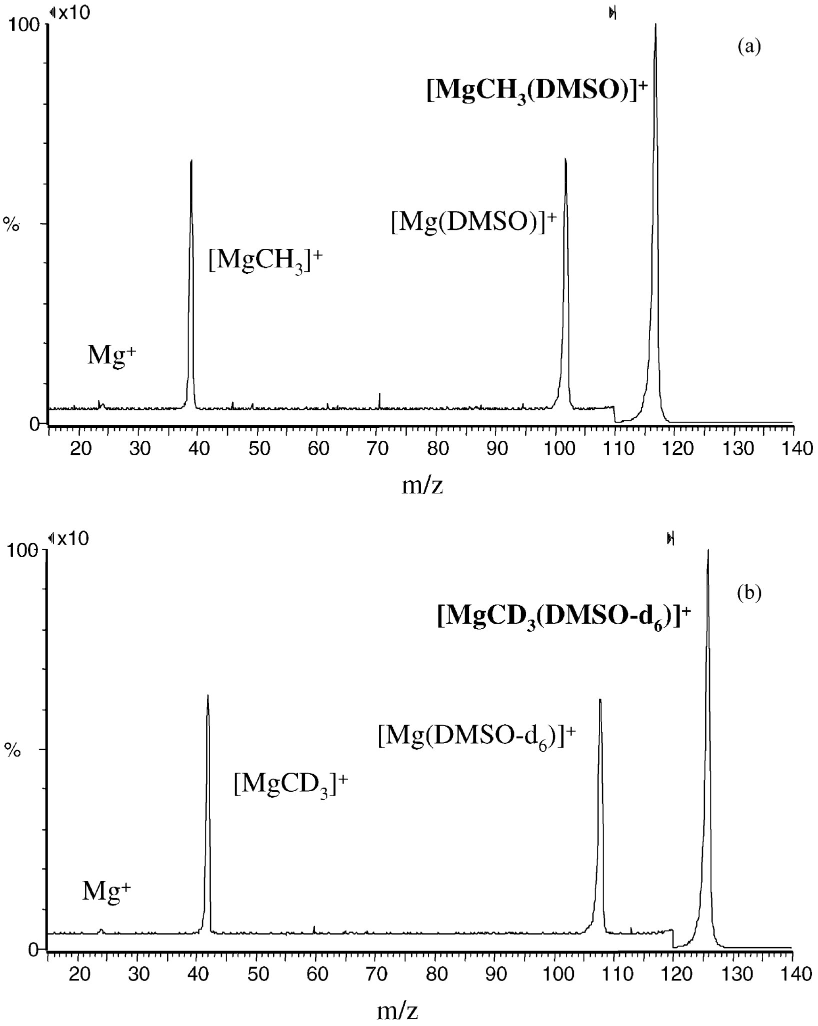

Fig. 10. The CAD spectra of (a) *m/z* 117 from aqueous $MgSO_4$/DMSO solutions; and (b) the analogous *m/z* 126 from aqueous $MgSO_4$/DMSO-d_6 solutions. $E_{Lab} = 40\,eV$; argon collision gas pressure 1×10^{-4} Torr. Parent ions, in bold, contain only ^{24}Mg and ^{32}S.

group originating from the DMSO ligand. Therefore, in addition to the decompositions described by Eqs. (20) and (21), a further decomposition, Eq. (22), occurs.

$$\underset{m/z\,117}{[MgCH_3(DMSO)]^+} \rightarrow \underset{m/z\,102}{[MgCH_3(CH_3SO)]^+} + CH_3 \tag{22}$$

The competition between the three reaction channels of activated $[MgCD_3(DMSO)]^+$ as a function of E_{Lab} is shown in Fig. 11. Loss of methyl is favored at the lowest energy, suggesting, since the entropy of activation should be roughly the same for direct ligand losses, that methyl is more weakly bound than DMSO. Demethylation of the DMSO ligand, although never accounting for more than 15% of total product yield is more pronounced at low than at high energy reminiscent of methyl loss in the doubly charged magnesium complexes. One significant difference is, however, that computation shows that the metal–ligand linkage in

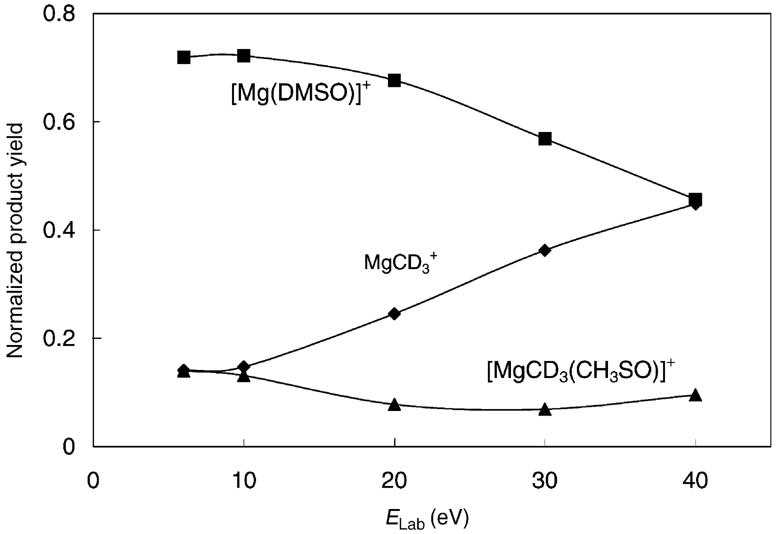

Fig. 11. The relative yields of product ions in the CAD spectrum of $[MgCD_3(DMSO)]^{2+}$ as functions of laboratory ion energy.

$[Mg(CH_3SO)]^+$ is via sulfur and not through oxygen as in $[Mg(CH_3SO)]^{2+}$. Mg^+, being softer than Mg^{2+}, prefers association with the soft S rather than the hard O site.

At 20 eV collision energy, the major product in the CAD spectrum of *m/z* 181, shown in Fig. 12(a), is *m/z* 117 i.e., loss of 64 u. When DMSO-d_6 was substituted for DMSO, the major product from *m/z* 190 was *m/z* 126, again a loss of 64 u. The same neutral loss in both cases confirms what was surmised from the ESI spectra, that no hydrogen was present in the neutral product, which can then be only S_2 or SO_2. The CAD spectrum of *m/z* 183, the isotopomer of *m/z* 181, in Fig. 12(b) has two major products, *m/z* 117 and 119, in the ratio 1:3.7. In the DMSO-d_6 system, the products *m/z* 126 and 128 from the analogous parent ion *m/z* 192 were in the ratio 1:3.4. The loss of both 64 and 66 u, as opposed to the single loss of 64 u from *m/z* 181 or 190, is due to the ions *m/z* 183 and 192 containing either ^{26}Mg and ^{32}S or ^{24}Mg and ^{34}S. The ratios of products are consistent with the value of 1:3.4 expected for the ratio of $[^{26}MgCH_3(^{32}S\text{-DMSO})]^+$ to $[^{24}MgCH_3(^{34}S\text{-DMSO})]^+$. The observed isotopic patterns of the groups of peaks 181 (69%), 182 (12%), 183 (17%), 184 (2%) in the DMSO ESI spectrum and 190 (69%), 191 (13%), 192 (16%), 193 (2%) in the DMSO-d_6 spectrum are consistent with the pattern 181 (68%), 182 (12%), 183 (17%), 184 (2%) computed from isotope natural abundances for the ion $[MgC_3H_9OS_2]^+$. The pattern is not consistent with an ion containing only one sulfur atom and the neutral product of mass 64 u must, therefore, be SO_2 and *m/z* 181 must be $[MgO(CH_3SO)(DMSO)]^+$ or $[MgCH_3(SO_2)DMSO)]^+$. The former seems the more probable, being consistent with both the propensity of the alkaline earth metal cations to form oxides and the readiness of a DMSO ligand to lose a methyl group.

The O atom in $[MgO(CH_3SO)(DMSO)]^+$ could arise from either DMSO or water. A water origin was investigated in separate experiments with aqueous solutions of magnesium salts containing no DMSO. The singly charged Mg-containing ions were of the series $[MgOH(H_2O)_n]^+$ with no evidence for a $[MgO(H_2O)_n]^+$ series. Mg^{2+} with both water and DMSO ligands also failed to show oxide formation in CAD experiments (vide supra). In nature, the reduction of DMSO by dimethyl sulfoxide reductase involves the oxidation of the enzyme at its molybdenum site and the release of dimethylsulfide [42] and, by a stretched analogy,

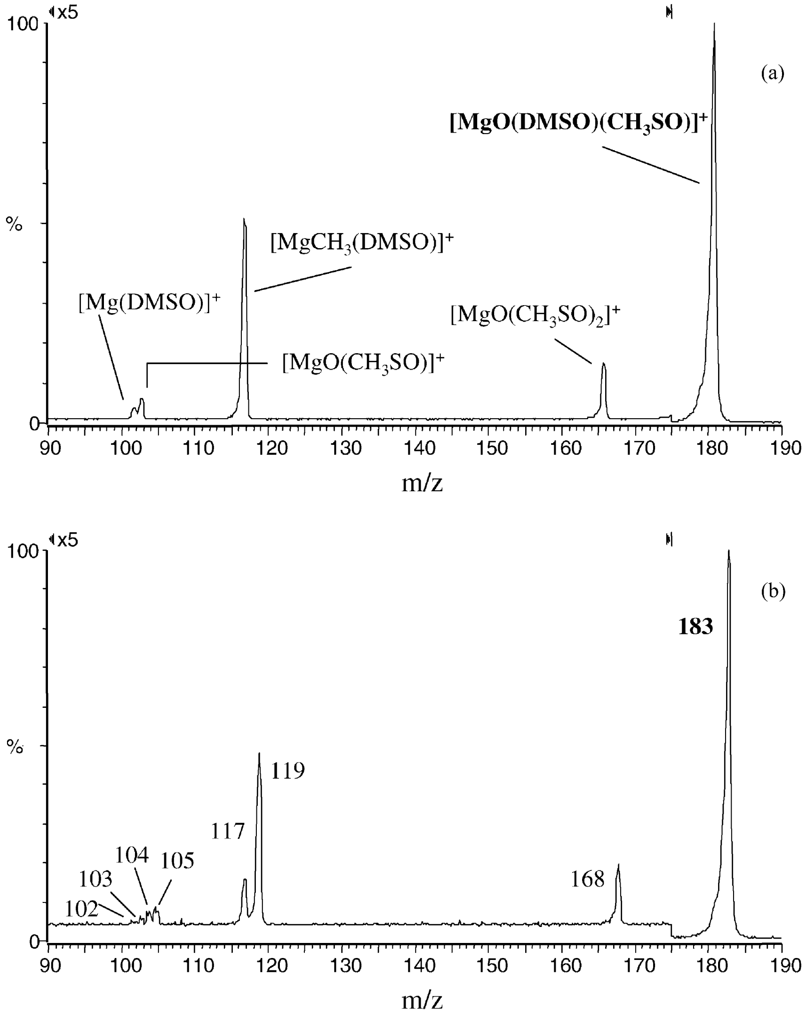

Fig. 12. The CAD spectra of (a) *m/z* 180, and (b) 183, obtained from aqueous solutions containing $MgSO_4$ and DMSO. The parent ions, in bold, are isotopomers, *m/z* 180 containing ^{24}Mg and ^{32}S only and *m/z* 183 containing ^{24}Mg and ^{34}S or ^{26}Mg and ^{32}S. $E_{Lab} = 40\,eV$.

$[MgO(DMSO)(CH_3SO)]^+$ might be formed in the present system by the loss of $(CH_3)_2S^+$ from, for example, $[Mg(DMSO)_2(CH_3SO)]^{2+}$. However, the CAD spectrum of this ion at low energy showed loss of CH_3SO giving $[Mg(DMSO)_2]^{2+}$ which dissociated at higher energy in the manner described earlier.

Parent ion spectra were obtained by scanning Q1 with Q2 focused on $[MgO(CH_3SO)(DMSO)]^+$. The hexapole collision cell was operated at potentials from −20 to −80 V but the only parent ions observed were of the series $[MgO(CH_3SO)(DMSO)_n]^+$ with $n = 2, 3$. The origin of these singly charged complexes is therefore not determined at this time. It is to be noted, however, that the formation of oxide in a charge reduction reaction in aqueous DMSO solutions is not peculiar to Mg^{2+}. We have, under suitable ion source conditions, found the series $[LaO(CH_3SO)(DMSO)_n]^{2+}$ ($n = 1$–8) in the ESI spectra of aqueous DMSO solutions containing La^{3+}

[43]. The lowest two members of this series are found to lose 64 u in CAD studies with no loss of charge. In addition, loss of methyl with no loss of charge is prevalent both from these ions and from $[La(DMSO)_n]^{3+}$. Kebarle and coworkers in their pioneering study of gas-phase triply charged metal complexes did not note the series $[LaO(CH_3SO)(DMSO)_n]^{2+}$ but instead described the presence of the two series $[LaOCH_3(DMSO)_n]^{2+}$ and $[LaOH(DMSO)_n]^{2+}$ [4]. The CH_3O ligand of the first series originated from the methanol used as solvent and the OH of the second series from either trace or added water. We may have observed members of the series $[LaOH(DMSO)_n]^{2+}$ but all were present in very low concentrations.

Loss of 15 u, a methyl group, from *m*/*z* 181 giving *m*/*z* 166 leads to the second most abundant CAD product. The loss of methyl was confirmed by the increase of three *m*/*z* units in the product ion when DMSO-d_6 was used. The product is presumed to be, by analogy with the ubiquitous methyl loss from the doubly charged ions, $[MgO(CH_3SO)_2]^+$. Loss of 78 u from *m*/*z* 181 gives a small peak at *m*/*z* 103 and loss of 79 u gives *m*/*z* 102. The loss of 78 u becomes a loss of 84 u with DMSO-d_6 i.e., *m*/*z* 103 is $[MgO(CH_3SO)]^+$. Similarly, *m*/*z* 102 becomes *m*/*z* 108. *m*/*z* 102 is, therefore, $[Mg(DMSO)]^+$. When the isotopic peak at *m*/*z* 183 in the $MgSO_4$/DMSO ESI spectrum is examined by CAD, four peaks are observed, *m*/*z* 102, 103, 104 and 105 (Fig. 12(b)). These are consistent with the above ion identifications, viz.: *m*/*z* 102, $[^{24}Mg(^{32}S\text{-}DMSO)]^+$; *m*/*z* 103, $[^{24}MgO(CH_3{}^{32}SO)]^+$; *m*/*z* 104, $[^{24}MgO(CH_3{}^{34}SO)]^+ + [^{26}MgO(CH_3{}^{32}SO)]^+$; and *m*/*z* 105, $[^{26}Mg(^{32}S\text{-}DMSO)]^+ + [^{24}Mg(^{34}S\text{-}DMSO)]^+$.

m/*z* 181, $[MgO(CH_3SO)(DMSO)_n]^+$, in losing SO_2 to give *m*/*z* 117, must transfer a methyl group from either one of its ligands to the metal. Since *m*/*z* 117 is $[MgCH_3(DMSO)]^+$, the methyl comes from the sulfinyl group.

$$\begin{aligned}&[(DMSO)MgO(CH_3SO)]^+\\&\quad\rightarrow [(DMSO)MgCH_3(SO_2)]^+\\&\quad\rightarrow [(DMSO)MgCH_3]^+ + SO_2\end{aligned}\tag{23}$$

5. Conclusions

DMSO readily forms doubly charged complexes, $[Mg(DMSO)_n]^{2+}$, when dilute aqueous solutions of DMSO containing magnesium salts are subject to electrospray ionization. Ions with $n = 4$ or larger, react upon collisional activation by loss of whole ligands i.e., desolvation. $[Mg(DMSO)_3]^{2+}$ loses DMSO only at low collision energies but loss of a methyl radical to give $[Mg(DMSO)_2(CH_3SO)]^{2+}$ becomes almost equally probable at the highest energies. The dominant CAD process for $[Mg(DMSO)_2]^{2+}$ is loss of a methyl radical, desolvation to give $[Mg(DMSO)]^{2+}$ is a minor reaction, and only occurs at high energy. The competitive reaction at high energy is loss of a second methyl to give $[Mg(CH_3SO)_2]^{2+}$. Charge reduction reactions do not predominate at any collision energy for any *n*. The dissociation of $[Mg(DMSO)]^{2+}$ was not examined. The calculated structures show that both the DMSO and CH_3SO ligands associate with the metal ion via oxygen through a mainly electrostatic bond.

The structures of several of the doubly charged mono- and di-ligated Mg^{2+} complexes have been computed and the observed CAD dissociations are consistent with their being determined by the reaction enthalpies. The reaction pathway for methyl loss was not investigated.

A singly charged ion that predominates at high cone potentials is $[MgO(DMSO)(CH_3SO)]^+$ which has a unique CAD dissociation. The transfer of methyl from the sulfinyl ligand to the metal allows the release of SO_2 as a neutral. The resulting $[MgCH_3(DMSO)]^+$ competitively loses methyl and DMSO. The origin of the oxide was not determined and could be from either water or DMSO.

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