$[Mg(thf)_4]^{2+}$: the first gas-phase evidence of a stable multiply charged metal–ligand unit

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The preparation and study of gas-phase clusters in the form of solvated multiply charged metal ions presents a considerable experimental challenge; these first results on $[Mg(thf)_4]^{2+}$ suggest that stability is due primarily to orbital overlap rather than electrostatic interactions.

At a microscopic level, the study of solvated singly charged metal ions in the gas phase has made a valuable contribution to our understanding of the structure and energetics of solvation in the bulk phase.[1,2] However, the majority of metal ions in solution form units which carry two or more positive charges, *e.g.* $[Cu(H_2O)_6]^{2+}$,[3] and the study of these species in the gas phase, represents a considerable experimental challenge.[4–6]

Difficulties arise because a doubly or triply charged metal ion in the presence of just a few solvent molecules is an inherently unstable unit: the first ionisation energy (E_i) for many organic solvents is typically 2–3 eV lower than the second E_i and considerably lower than the third E_i of most metals. This marked difference in ionisation energy means that an isolated multiply charged metal ion is unlikely to survive more than a few collisions with a possible solvent molecule before charge transfer occurs. Since the latter process is strongly exothermic, it becomes impossible to 'grow' clusters containing multiply charged metal cations, because there is no opportunity for them to be stabilised by solvation prior to a change in oxidation state.

Significant experimental advances have been made in the production of clusters incorporating dipositive metal ions by Kebarle and coworkers[4–6] using electrospray[7] and by Schmelzeisen–Redeker *et al.*[8] using thermospray. However, these techniques are limited to studies of those types of ions already present as electrolytes in solution and the actual production of multiply charged solvated species appears to be sensitive to the nature of the salt used.[5] Reported here are results from a new technique whereby ionisation of the metal takes place *after* it has been embedded in a solvent environment which, in this case, is tetrahydrofuran (thf). The newly created multiply charged species is thus able to gain immediate benefit from the presence of a surrounding shell of solvent molecules and therefore emerges as a stabilised gas-phase cluster ion.

Detailed descriptions of the experimental techniques used to generate and detect cluster ions have been published before;[9,10] the initial formation of neutral thf clusters requires conditions very similar to those used in previous experiments involving benzene.[11] Magnesium atoms are 'picked up' from an oven by thf clusters prior to entering the ion source of a mass spectrometer (VG ZAB-E) where they are subsequently ionised by 70 eV electron impact. Although their absolute intensities are quite low in comparison to the total ion current, sufficient doubly charged ions are generated to allow for quantitative experiments to be undertaken. Fig. 1(*a*) shows the relative intensities of $[Mg(thf)_n]^{2+}$ plotted as a function of the number of thf molecules. Two sets of data are shown, one corresponds to clusters containing the most abundant, ^{24}Mg isotope and for the purposes of conformation, measurements were also made on clusters containing ^{25}Mg. The ion intensities do not follow the natural isotopic ratios because there is a small amount of $[Mg(thf)_nH]^{2+}$ formation which can influence the intensity of $[^{25}Mg(thf)_n]^{2+}$ clusters for the same value of n. The presence of an intense ion of unknown composition prevented the measurement of a result for $[^{24}Mg(thf)_2]^{2+}$. It is quite clear from Fig. 1(*a*) that the most intense ion corresponds to the complex $[Mg(thf)_4]^{2+}$ which commands an intensity twice that of even its immediate neighbours. To confirm that the intensity fluctuations are not due just to variations in the way thf molecules are accommodated, the experiment was repeated for singly charged $[Mg(thf)_n]^+$ cluster ions. These results are shown in Fig. 1(*b*), where it can be seen that the pattern of behaviour shown by $[Mg(thf)_n]^{2+}$ cluster ions is not reproduced.

There are two factors contributing to the size dependence seen in Fig. 1(*a*). First, the minimum number of thf molecules necessary to stabilise the double charge is two; the complex $[Mg(thf)]^{2+}$ appears to be unstable with respect to charge transfer. In addition, the intensities of clusters with $n = 2$ and 3 will be depleted *via* the loss of molecules and eventual charge transfer. Secondly, the type of experiment used to create the ion complexes is strictly non-equilibrium, hence, clusters of all sizes are unstable with respect to the loss of individual thf molecules. Therefore, an initial (arbitrary) size distribution will automatically gravitate downwards to give, in the absence of

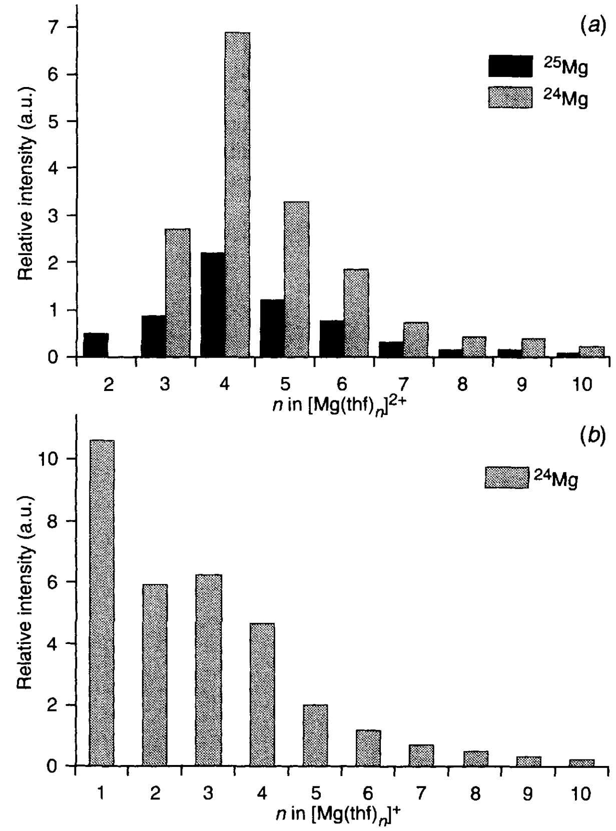

Fig. 1 (*a*) Relative intensities of $[Mg(thf)_n]^{2+}$ complexes plotted as a function of n. Results are shown for two isotopes of magnesium; (*b*) as for (*a*), but for singly charged $[^{24}Mg(thf)_n]^+$ complexes.

any additional constraints, a distribution of the form shown in Fig. 1(*b*). However, if one or more members of a distribution are particularly stable, then they are found to gain in intensity at the expense of their immediate neighbours. This effect is known to be responsible for the observation of stable 'magic number' atom combinations in rare-gas cluster ions,[9] and we believe that it also accounts for the enhanced intensity of $[Mg(thf)_4]^{2+}$ seen in Fig. 1(*a*).

There is a very extensive catalogue of crystallographic and spectroscopic data on the structures of (tetrahydrofuran)magnesium(II) complexes.[12–16] In the majority of cases, the central unit is $[Mg(thf)_4]^{2+}$ in a tetragonal arrangement and charge stabilised with either two Br or two Cl atoms as counter ions to give an octahedral complex.

A detailed analysis of the structures of these complexes,[12] suggests that Mg^{2+} prefers to be coordinated to sp^3-hybridized oxygen lone pairs in an arrangement which combines orbital overlap with electrostatic interactions, the latter probably being dominated by ion-induced dipole (polarisation) interactions. The observation of a stable $[Mg(thf)_4]^{2+}$ unit in the gas phase provides a mechanism for accessing the relative significance of these two contributions to bonding. If purely electrostatic considerations were important, then it might be expected that the structural relaxation which accompanies formation in the gas phase, would favour a stable $[Mg(thf)_6]^{2+}$ unit with octahedral symmetry similar to that seen, for example, in bulk phase $[Mg(thf)_4]^{2+}(Br^-)_2$. However, if orbital overlap between Mg^{2+} and the eight lone-pair electrons of the four thf ligands has more influence on structure and/or stability, then that same factor will be important in both the bulk and gas phase and $[Mg(thf)_4]^{2+}$ will always be seen as the stable unit. If this idea is extended to the singly charged ions, then $[Mg(thf)_3]^+$ might be the nearest ion to achieving a stable eight-electron configuration, and there is some evidence of this to be seen in Fig. 1(*b*).

In a final experiment, the MIKE technique[17] was used to examine the unimolecular and collision-induced chemistry of small $[Mg(thf)_n]^{2+}$ cluster ions. As might be expected from the discussion given above, the principal unimolecular reaction path is the loss of a single thf molecule. However, it is under conditions of collisional activation (CA) that the following more interesting reaction is observed [eqn. (1)] (CA is promoted by the introduction of 10^{-6} Torr of air into a collision cell located within the flight path of the ions).

$$[Mg(thf)_3]^{2+} \longrightarrow [Mg(thf)_2(CH_2O)]^{2+} + C_3H_6 \qquad (1)$$

The reaction corresponds to a ring-opening process which appears to leave the metal ion coordinated with the same number of oxygen atoms; but with one which is now sp^2 rather than sp^3 hybridised. The same reaction is observed following the CA of $[Mg(thf)_4]^{2+}$, but is now in competition with the loss of a thf molecule. Both complexes exhibit limited electron transfer in the form of thf^+ loss.

Of particular interest in these experiments has been the observation of a very strong gas-phase signal corresponding to formation of the complex $[Mg(thf)_4]^{2+}$, which is also known to occupy a pivotal position in many stable organometallic complexes. We believe this to be the first example of a stable gas-phase metallic complex being found to have a direct bulk phase analogue.

References

1 P. Kebarle, *Annu. Rev. Phys. Chem.*, 1977, **74**, 1466.
2 R. G. Keesee and A. W. Castleman Jr., *J. Phys. Chem. Ref. Data*, 1986, **15**, 1011.
3 F. A. Cotton and G. W. Wilkinson, in *Advanced Inorganic Chemistry*, Wiley, London, 1988.
4 P. Jayaweera, A. T. Blades, M. G. Ikonomou and P. Kebarle, *J. Am. Chem. Soc.*, 1990, **112**, 2452.
5 A. T. Blades, P. Jayaweera, M. G. Ikonomou and P. Kebarle, *J. Chem. Phys.*, 1990, **92**, 5900.
6 A. T. Blades, P. Jayaweera, M. G. Ikonomou and P. Kebarle, *Int. J. Mass Spectrom. Ion Proc.*, 1990, **102**, 251.
7 M. Yamashita and J. B. Fenn, *J. Phys. Chem.*, 1984, **88**, 4451.
8 G. Schmelzeisen-Redeker, L. Bütfering and F. W. Röllgen, *Int. J. Mass Spectrom. Ion Proc.*, 1989, **90**, 139.
9 P. G. Lethbridge and A. J. Stace, *J. Chem. Phys.*, 1989, **89**, 4062.
10 J. F. Winkel, C. A. Woodward, A. B. Jones and A. J. Stace, *J. Chem. Phys.*, 1995, **103**, 5177.
11 A. B. Jones, R. Lopez-Martens and A. J. Stace, *J. Phys. Chem.*, 1995, **99**, 6333.
12 P. R. Markies, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets and A. L. Spek, *Adv. Organomet. Chem.*, 1991, **32**, 147.
13 R. Sarma, F. Ramirez, B. McKeever, Y. F. Chaw, J. F. Marecek, D. Niermann and T. M. McCaffery, *J. Am. Chem. Soc.*, 1977, **99**, 5289.
14 P. Sobota, T. Pluzinski and T. Lis, *Polyhedron*, 1984, **3**, 45.
15 K. Handlir, J. Holecek and L. Benes, *Collect. Czech. Chem. Commun.*, 1985, **50**, 2422.
16 P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1162.
17 R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, in *Metastable Ions*, Elsevier, Amsterdam, 1973.

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