A Gas-Phase Study of the Coordination of Mg^{2+} with Oxygen- and Nitrogen-Containing Ligands

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Abstract: An experimental study of the stability and coordination of oxygen- and nitrogen-containing ligands in association with Mg^{2+} in the gas phase has been undertaken. The ligands chosen exhibit a wide range of physical properties in terms of their ionization energies, dipole moments, and polarizabilities, and a simple electrostatic model reveals a semiquantitative trend between these properties and the ability of each ligand to stabilize Mg^{2+}. The model clearly demonstrates why water is extremely effective at stabilizing Mg^{2+}, and in this respect, CO$_2$ also proves to be a good ligand. Evidence of a discrete first solvation shell is apparent only for those ligands which do not display hydrogen bonding. For water, methanol, and ethanol, hydrogen bonding leads to extended solvation units for which the boundaries are less obvious. However, for more complex alcohols, steric interactions appear to negate the influence of hydrogen bonding. Discrete solvation shells are observed for most aprotic ligands, and the optimum coordination number is 4. However, there is some slight variation in this value, mainly as a consequence of ligand size. Assuming Mg^{2+} to be a hard Lewis acid, the results are used to order the ligands in terms of how effective they are at stabilizing Mg^{2+} in their role as hard Lewis bases. Evidence of the first gas-phase Mg^{2+} bidentate metal complex is also provided.

Introduction

The solvation and coordination of Mg^{2+} in both aqueous and biologically related environments has been the subject of numerous theoretical studies.[1−18] Several groups have investigated the behavior of Mg^{2+} in terms of the structure and binding energies of various biologically significant ligands in competition with water.[1−5] Other calculations of a related nature have concentrated primarily on Mg^{2+}/water complexes[6−14] and have frequently addressed the specific role hydrogen bonding plays in determining local structure. Studies by Bock et al.[16−18] have combined theory and experiment by comparing calculations on Mg^{2+} coordination with protein crystallography data. What links many of these calculations is the use of a discrete cluster model to represent the first solvation shell, on the assumption that such a unit will reproduce much of the essential thermodynamics and stereochemistry.

In solution, metal ions carrying more than one positive charge are frequently represented in the form of discrete complexes between solvent and ion: for example, [Cu(H$_2$O)$_6$]$^{2+}$ or [Ni(NH$_3$)$_6$]$^{2+}$.[19] Such units denote a distinction between the primary and subsequent solvation shells; however, they also acknowledge an implicit relationship between ion and solvent, whereby it is recognized that isolated ions, such as Cu^{2+}, frequently cannot coexist in the presence of a single solvent molecule. Any consideration of the difference between the second ionization energy (IE) of a typical metal and the first IE of an organic solvent will immediately show that charge transfer should take place on contact. The encounter between a single molecule and a doubly charged cation has been modeled by Weisshaar and co-workers,[20,21] and various scenarios were identified from potential energy curves representing possible charge-transfer processes, some of which were accompanied by chemical reactions. That multiply charged metal ions can become stable in the presence of several solvent molecules illustrates the fact that the ions are intimately coupled to their immediate environment in a way which is not necessarily true of singly charged ions. However, charge transfer does still take place, and Marcus has given a quantitative analysis of this process in relation to ions in solution.[22]

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In at least one very important respect, the study of small, multiply charged metal complexes in (gas-phase) isolation is more closely related to biological coordination chemistry than results obtained from experiments undertaken in bulk solvents. The inner-shell complexes of the type used in calculations and generated in gas-phase experiments represent comparatively rigid structures, which present (to the ion) an immediate environment where the dielectric constant is very low ($\epsilon \leq 4$).[1,4] Likewise, metal ions are held rigid by their association with a few water molecules and functional groups, such as carboxylates and phosphates, emanating from protein residues.[23,24] In this respect, the situation presented by a protein site must fall somewhere between the fully coordinated solvent environment and that identified for single molecule encounters. There should be sufficient electron donation from the site to control the oxidation state of the metal ion, but at the same time, the latter is not exposed to the full dielectric properties of a bulk solvent such as water.

In attempting to relate solvent behavior to the properties of the individual molecules, many of the solvent complexes could be viewed as components of a Lewis acid−Lewis base system, with the "hard" Mg^{2+} acid preferring to bind to "hard" nonpolarizable ligands, such as water.[25−27] A further (very) important consideration, particularly from the viewpoint of adopting a "cluster-like" model of ion solvation,[12] is the uniqueness of the first shell in terms of its structural separation from the properties of the bulk solution.[28] The latter is assumed to start at the boundary between the first and second solvation shells, and for the first solvation shell to be a distinct structural entity requires the ligands to have long residence times. In addition, the influence of the charge on the cation should be minimal at the periphery of the shell. The exchange times for water molecules in the primary solvent shell surrounding Mg^{2+} are known from experiment to be comparatively long;[29] however, calculations show that the high charge density which contributes to this effect also leads to enhanced hydrogen bond strengths in the second solvation shell.[11]

Experiments on $[Mg(L)_n]^{2+}$ clusters for many of the ligands (L) considered in the above calculations have yet to be undertaken. However, significant progress toward obtaining quantitative information on $Mg^{2+}−H_2O$ binding energies has been made by Kebarle, Blades, and co-workers[30−32] and Williams and co-workers.[33,34] Comparisons between experiment and theory on a wider range of ligands have been undertaken by Bock et al.[16−18] using a crystallographic database to compare the preference of Mg^{2+} for oxygen-, nitrogen-, and sulfur-based

ligands. The qualitative conclusions are that Mg^{2+} has an optimum coordination number of six, and the ion prefers attachment to ligands containing oxygen rather than nitrogen.[18] A similar conclusion regarding coordination number was reached by Matwiyoff and Taube following magnetic resonance experiments on Mg^{2+} in solution.[35] In the context of organo-metallic chemistry,[36] then, it is frequently observed that Mg(II) complexes adopt four-fold coordination, which is probably a result of steric interactions associated with the bulky groups used to stabilize the ion.

Restrictions on the part of detailed experimental work on multiply charged metal−ligand complexes may be associated with the fact that their preparation and study in the gas phase presents a range of technical problems. First, it is necessary to generate the species in a way that does not rely on single-molecule nucleation about an ion core, a situation which is quite different from a number of the techniques developed to study solvated singly charged ions.[37,38] Second, high-resolution mass spectrometry may be required to provide accurate mass iden-tification and to allow for the isolation and interrogation of individual ion−solvent complexes. Multiply charged ions will often appear at fractional m/z values, and some complexes have been observed to lose H and H_2.[39,40]

Weisshaar and co-workers reported some of the first inves-tigations into the reactions of isolated doubly charged metal ions,[20,21] as did Freiser and co-workers.[41] As far as metal ion−solvent complexes are concerned, results have been reported by Kebarle and co-workers,[30−32,42,43] Schmelzesen-Redeker et al.,[44] and, more recently, Posey and co-workers[45,46] and Williams et al.[33,34,47] All the examples discussed by these groups have been prepared using either electrospray or thermospray, both of which require that the ions of interest be present in solution prior to their appearance in the gas phase. As an alternative to these methods, we have shown in a series of recent papers that the "pick-up" technique can be used to prepare stable, multiply charged complexes from such metals as copper,[48,49] silver,[50] gold,[51] holmium,[52] magnesium,[39,53] strontium,[40] manganese,[54]

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and chromium,[54] in number densities that are high enough for quantitative experiments, such as the study of their UV charge-transfer spectroscopy.[55] None of the techniques available for preparing multiply charged complexes are, as yet, able to perform systematic measurements of binding energies across the accessible size and ligand range; however, Kebarle and co-workers have been successful in the determination of thermodynamic quantities for larger ($n \geq 5$) $[Mg(H_2O)_n]^{2+}$ complexes,[30-32] as have Williams et al. for a range of doubly charged metal−water complexes.[33,34,47]

Apart from crystallographic data, there is currently no experimental information available on the stability of Mg^{2+} in association with many of the ligands that may be of interest in biological systems. Reported here are the results of a new series of experiments on magnesium where gas-phase complexes have been prepared between Mg^{2+} and a broad range of solvent molecules. Thus far, we have presented results on CH_3OH and THF (tetrahydrofuran) as solvents,[39,53] and in the case of the latter, the most stable gas-phase species was found to be an analogue of a solid-state Mg^{2+} complex.[53] Our intention has been to extend the range of solvents in an attempt to identify those factors responsible for stability and coordination. To achieve that objective, 20 potential ligands have been studied, ranging from the very simple, e.g., NO, CO_2, through to more complex bidentate ligands. Not all of the molecules studied formed complexes, but failures were considered to be as instructive as successes in the sense that some general pattern may emerge as to the conditions necessary for the formation of stable $[MgL_n]^{2+}$ units in the gas phase. A simple electrostatic model has been used to interpret the data, and this provides some insight into the factors responsible for the success of water as a ligand for Mg^{2+} in biological systems.[24] A qualitative pattern can be identified for many of the other ligands in terms of their ability to stabilize the magnesium dication as a function of specific physical properties. Evidence for the existence of particular complexes, together with semiquantitative information on their primary coordination numbers, should help to support and motivate further theoretical studies of these systems.

Experimental Section

A detailed description of the general instrumentation used for generation, resolution, and detection of the cluster beam has been provided in previous publications.[39,50] Briefly, neutral clusters were formed via the adiabatic expansion of a solvent/argon mixture through a 200-μm pulsed supersonic nozzle. Midway between the expansion chamber and the mass spectrometer (VG ZAB-E), the cluster beam passed over the mouth of a high-temperature effusion cell (DCA Instruments, EC-40-63-21) equipped with a crucible of pyrolytic boron nitride. Several sources of magnesium vapor were tested (chippings, rod, and ribbon), and all forms proved capable of providing magnesium vapor for up to 8 h of continuous operation.

All of the experiments conducted using the "pick-up" technique have shown that, for a given ligand, L, the presence of clusters of the form Ar_nL_m in the beam is essential to the success of the technique. The formation of neutral metal/solvent clusters then follows from collisions between metal atoms and argon/solvent clusters, with the energy from the collision being dispersed by the ejection of argon atoms. Del Mistro and Stace[56] have presented a theoretical molecular dynamics description of the pick-up process that provides some insight into how the mechanism may operate. The neutral clusters were ionized by 100-eV
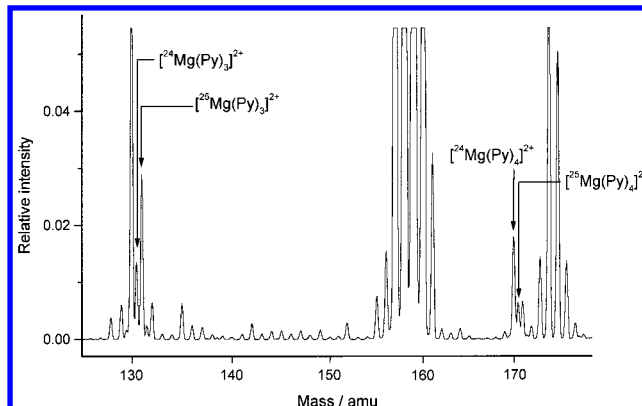
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Figure 1. Short section of a mass spectrum recorded following the formation of $[Mg(pyridine)_n]^{2+}$ complexes via the pick-up technique. Peaks due to both ^{24}Mg and ^{25}Mg have been identified.
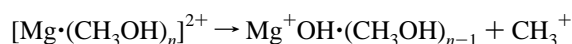
electrons; a process that is sufficiently violent to remove any evidence of Mg/ligand/argon clusters from the ion beam. There was also no evidence of ionic clusters containing more than one metal atom.

A shutter at the exit of the effusion cell was used to confirm the identity of clusters containing magnesium. Where a survey was performed of the relative intensities of parent ions of a given series, the difference was taken between the signal intensity with the shutter open and closed. This approach removed any contribution from background signal that was not dependent on material originating from the effusion cell. Figure 1 shows a short section of a typical mass spectrum, and this particular example, $[Mg \cdot (pyridine)_n]^{2+}$, serves to illustrate some of the problems encountered in these types of experiments. The ideal situation is for the m/z value for each doubly charged ion to be half-integer; under these circumstances, the possibility of overlap with another ion having the same m/z value is reduced significantly when compared with integer m/z values, the primary sources of overlap being singly charged pyridine and pyridine/argon cluster ions. The nominal m/z values for the ions shown are as follow: $[^{24}Mg \cdot (pyridine)_3]^{2+} = 130.5$; $[^{25}Mg \cdot (pyridine)_3]^{2+} = 131$; $[^{24}Mg \cdot (pyridine)_4]^{2+} = 170$; $[^{25}Mg \cdot (pyridine)_4]^{2+} = 170.5$. The isotope ratios for magnesium are $^{24}Mg:^{25}Mg:^{26}Mg = 79:10:11$, which means that ^{24}Mg should provide the most accurate data, but for all ligands of even-mass and even numbers of odd-mass ligands, measurements were susceptible to the presence of underlying peaks. In practice, a combination of measurements from both ^{24}Mg and ^{25}Mg has been used to obtain the intensity information given in Figures 3 and 4, below, and in Table 1. Where fragmentation data are required, these have been recorded, where possible, using whichever isotope falls at a half-integer m/z value. Separate intensity measurements taken at this time are used to confirm the data presented in Table 1.

Fragmentation processes for several of the complexes discussed here were examined in the presence of ~10^{-6} mbar of air as a collision gas. The fragments arising from CID were identified by scanning the ESA in the form of mass-analyzed ion kinetic energy (MIKE) scans.[57] These scans were performed on doubly charged ions with kinetic energies of 10 keV, which allowed for straightforward detection and verification of fragment ions resulting from Coulomb explosion.

Results and Discussion

The principal results to emerge from the present experiments are, first, the minimum number of ligands necessary to stabilize Mg^{2+}, n_{min}. As will be seen, some ligands are very effective at stabilizing the ion, whereas others readily undergo reactive charge transfer via, for example, a hydrolysis reaction at small values of n:[39]

$$[Mg \cdot (CH_3OH)_n]^{2+} \rightarrow Mg^+OH \cdot (CH_3OH)_{n-1} + CH_3^+$$

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Table 1. Data Derived from Intensity Distributions Recorded for a Range of $[Mg\cdot L_n]^{2+}$ Complexes, Together with Various Physical Properties Associated with the Ligands, L^a

complex	$n_{min}{}^b$	$n_{max}{}^c$	α (A³)^d	μ (D)^e	IE (eV)^f
$[Mg(CO_2)_n]^{2+}$ carbon dioxide	2	4	2.63		**13.8**
$[Mg(H_2O)_n]^{2+}$ water	2	4−6	1.48	1.85	**12.6**
$[Mg(CH_3CN)_n]^{2+}$ acetonitrile	1	4 (6)^g	4.40	3.92	**12.2**
$[Mg(C_4H_9NH_2)_n]^{2+}$ butylamine	2	4	**13.5**	1.0	9.4
$[Mg(C_5H_{10}O)_n]^{2+}$ 2-pentanone	2	4	**9.93**		9.38
$[Mg(C_4H_5N)_n]^{2+}$ pyrrole	2	4	**9.27**	4.22	8.64
$[Mg(C_5H_5N)_n]^{2+}$ pyridine	2	4	**9.18**	2.21	9.25
$[Mg(THF)_n]^{2+}$ tetrahydrofuran	2	4^h	~**9**	1.75	9.2
$[Mg(\{CH_3CH_2\}_2O)_n]^{2+}$ diethyl ether	2	3	**9.0**	1.15	9.4
$[Mg(C_4H_8O)_n]^{2+}$ 2-butanone	2	4	**8.13**	2.78	9.51
$[Mg(NH_3)_n]^{2+}$ ammonia	3	4	2.48	1.47	10.16
$[Mg(CH_3OH)_n]^{2+}$ methanol	2	5−10^i	3.23	1.71	10.8
$[Mg(C_2H_5OH)_n]^{2+}$ ethanol	3	4 (6, 8)^g	5.41	1.69	10.47
$[Mg(C_3H_7OH)_n]^{2+}$ n-propanol	3	4^j	6.74	1.58	10.2
$[Mg(\{CH_3\}_2CO)_n]^{2+}$ acetone	3	4 (6)^g	6.39	2.88	9.7
$[Mg(penta-2,4-dione)_n]^{2+}$	1	2	10.5		8.85
$[Mg(\{CH_3\}_2N-\{CH_2\}_2-N\{CH_3\}_2)_n]^{2+}$ ethylene diamine	k				7.6
$[Mg(DMSO)_n]^{2+}$ dimethyl sulfoxide	k			3.96	9.1
$[Mg(NO)_n]^{2+}$ nitric oxide	k			1.70	0.16

^{a} Boldface type is used to highlight physical properties of the ligands that considered to make an important contribution to the stability of a particular complex. These data are to be compared with the ionization energies of Mg and Mg⁺ at 7.65 and 15.03 eV, respectively. ^{b} Minimum number of ligands required to stabilize Mg²⁺. ^{c} Number of ligands present in the ion of maximum intensity. ^{d} Polarisability of the ligand. ^{e} Dipole moment of the ligand. ^{f} Ionization energy. ^{g} Secondary maxima or shoulder in the intensity distribution. ^{h} A complete intensity distribution can be found in ref 53. ^{i} A complete intensity distribution can be found in ref 39. ^{j} A complete intensity distribution can be found in ref 67. ^{k} These ligands failed to form stable complexes with Mg²⁺.

Although the metal ion in the product is still effectively Mg-(II), its chemical and coordination properties are clearly quite different as Mg⁺OH rather than Mg²⁺. The formation of Mg⁺-OH will put electron density into the 3s orbital of the magnesium ion, and this will influence any interaction with potential ligands. The second experimental measurement undertaken is that of the value of n which has the highest intensity for a given $[Mg(L)_n]^{2+}$ complex, n_{max}. In many instances, it has been found that this number corresponds to the optimum coordination number of an ion; however, to make such a connection it is necessary to bear in mind the various effects that can contribute to ion intensity in this type of experiment. There are two competing factors responsible for the shape of an ion intensity distribution. First, there are only a few instances of $[MgL_n]^{2+}$ clusters being observed where $n_{min} = 1$ (see below). This absence is due to the instability referred to in the Introduction. For small values of n, there are insufficient solvent molecules present to stabilize the doubly charged unit, with the result that charge transfer occurs and the cluster breaks up due to Coulomb

explosion. Such processes are frequently accompanied by the breaking of covalent bonds within solvent molecules, and in the case of alcohols, for example, MgOH⁺·(L_n) is often seen as a reaction product.[39] Some of these reactions are observed as a result of metastable (unimolecular) decay, whereas other processes, where it is assumed there may be a barrier, can be promoted by the collisional activation of small $[MgL_n]^{2+}$ clusters. It has been proposed that some of the reactions proceed via anion transfer:[39] for example, those of OH⁻ or CH₃O⁻. As n increases, the complexes become more stable; however, at this stage a second contribution to the shape of each distribution becomes important, and this is the natural decline in intensity which typically accompanies clusters as their size increases. A typical mass spectrum of atomic or molecular clusters (consisting primarily of singly charged ions) will show an almost exponential decline in intensity as a function of size, a feature which makes it easier to distinguish fluctuations due to the presence of particularly stable or "magic number" structures.[58] Changes in experimental conditions, such as gas pressure, can have a significant influence on the shape of an intensity distribution; however, "magic numbers" are inclined to survive minor distortions. Given that the size range covered in these experiments is typically limited to $n \le 10$, the important contributions are going to come primarily from development of the first solvation shell surrounding Mg²⁺.

Table 1 presents a summary of all the ligand systems studied, both successful and unsuccessful. The latter groups have been included in order that their physical characteristics may contribute to a discussion of those interactions responsible for the formation of a stable $[MgL_n]^{2+}$ complex. Listed in the table are (i) n_{max}, (ii) n_{min}, (iii) the available polarizabilities (α) and dipole moments (μ) of the ligands, and (iv) the ionization energies of the ligands. Some of the ligands tested, NO for example, were not expected to form stable complexes; however, in this context it is interesting to note the recent observation of stable Mg²⁺·Ar$_n$ cluster ions by Velegrakis and Luder.[59] Mg²⁺·Ar$_n$ clusters are stable because the second IE of magnesium is less than that of a single argon atom; therefore, the two positive charges should reside predominantly on the metal atom. Although the first ionization energies of argon clusters are known to be lower (~14.25 eV) than that of a single atom,[60] it is recognized that charge transfer in such systems occurs between single atoms,[61] and that any collective modification to the energetics due to cluster formation has little influence on the process. The pick-up technique yields quite intense signals of Mg²⁺·Ar$_n$ clusters; however, because there is nothing unusual about their stability, these ions are not discussed further.

There is some overlap between the ligands listed in Table 1 which form stable complexes and those Mg⁺−X dimer ions for which Operti et al.[62] recorded thermodynamic data; however, there is no obvious correlation between their binding energies and the coordination numbers presented here. In both Mg⁺ and Mg²⁺, electrostatic ion−dipole and polarization or induced dipole interactions are going to make the dominant contribution to bonding; however, there is also the possibility of a covalent interaction via the delocalization of electron density from occupied ligand orbitals into the empty 3p and 3s orbitals of Mg²⁺ or, in the case of Mg⁺, the partially filled 3s orbital. In

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the latter, electron repulsion will limit delocalization, but that will not be the case for Mg^{2+}. Thus, the ability of a ligand to donate electrons could be an important consideration in our analysis of the data presented here.

In the context of electron donation, some of the complexes could be viewed as components of a Lewis acid−Lewis base system. For example, highly polarizable electron-rich ethers will act as bases to be complemented by Mg(II), which would perform the role of a Lewis acid. Thus, an organomagnesium compound might be expressed as $R_mMg \cdot nL$,[36] where L represents a weakly bound ligand in the form of a Lewis base, such as diethyl ether or THF, and R is an anionic counterion required to balance the charge on Mg(II). Coordination around the magnesium atom would be driven, in part, by the need of Mg-(II) for donated electrons, but mainly by steric considerations associated with the accommodation of bulky ligands L.[36] $m + n$ is equal to at least 4 for unidentate ligands. Thus, many of the complexes discussed here could be considered as the Mg-(II)·nL component of an organomagnesium compound, but with the flexibility to accommodate more ligands because of the absence of counterions.

As a function of size, it is evident from Table 1 that a qualitative trend exists. The smaller ligands, such as water and methanol, coordinate five (possibly six) molecules to form a stable first shell. As the ligands increase in size, n_{max} drops to 4, but with some evidence of a step or shoulder at 6, as seen, for example, with acetonitrile and acetone. Thus, both four-fold and six-fold coordination are possible, with the former appearing to be the preferred option as the ligands increase in size. What the experiments do not reveal is whether the four-coordinate complexes are tetrahedral or square-planar. Mg^{2+} has a closed-shell electron configuration and also has no p or d electrons to be taken into account when it interacts with ligands. Therefore, any structural considerations are going to be determined solely by the bulky nature of the ligands, and under those circumstances, tetrahedral coordination will probably be favored over square-planar.[36] The six-fold coordinate complexes most probably have octahedral symmetry. In the case of very bulky ligands, such as diethyl ether, the optimum coordination number, n_{max}, is seen to drop to 3.

The stable complexes in Table 1 appear to fall into three distinct categories. First, there are those formed with molecules that have high IEs (>12 eV), such as water, carbon dioxide, and acetonitrile. For these ligands, the difference between their IE and that of Mg(I) is small, and so the energy required to stabilize the complex is also small. These complexes all have n_{min} values of either 1 or 2. In the second category, there are complexes between Mg^{2+} and molecules with high polarizabilities (>8 Å³). Although their IEs may be comparatively low, these species are stable because of a strong ion−induced dipole interaction. Examples here include pyridine, diethyl ether, and butylamine, and these all have n_{min} values of 2. Finally, there is a group of complexes that are stable because the physical constants for the molecules concerned are all moderately large; i.e., the combination of ion−dipole and ion−induced dipole interactions is sufficient to counteract the difference in ionization energies between Mg(I) and L. Molecules falling into this last category include the alcohols and THF, and most of the n_{min} values are 3.

Model Calculations of $[Mg \cdot L_n]^{2+}$ Stability. From the experimental data, it is evident that within the range of ligands studied there are trends which appear to correlate with particular physical properties. To quantify our understanding of these patterns of behavior, an attempt has been made to account for the stability, with respect to charge transfer, of each $[Mg \cdot L_n]^{2+}$ complex as a function of the number of ligands, n. Such a calculation requires two important energy terms to be taken into consideration: (a) the absolute stability of $[M \cdot L_n]^{2+}$ relative to the charge-transfer $[M^+ \cdot L_n^+]$ dissociation limit, and (b) the crossing point of the two surfaces. In the absence of detailed ab initio data covering all of the ligand/metal combinations listed in Table 1, a simple model based on electrostatic interactions is proposed, which utilizes the polarizabilities and, where appropriate, the dipole moments of the constituent ions and molecules.[63] The model makes the following assumptions: (i) there is a scalar quantity, r, that defines the M−L distance, and no account is taken of other geometric factors; (ii) L has a point dipole (μ) and an isotropic polarizability (α) (all energies are represented by point interactions); (iii) there are no attractive L−L terms, so that for dipolar ligands the geometry of ML_2 is linear (for nonpolar ligands this will be a poor approximation); (iv) the polarizability and dipole moment of L^+ and L are the same, which is certainly not the case for small ligands, such as H_2O; (v) the polarizabilities of M^+ and M^{2+} are the same. The only other relevant parameter is Δ, which is the difference in ionization energy between M^+ and L. Data relevant to the above calculations are listed in Table 1.

Taking charge to be in units of electrons, dipole moment in debye, polarizability in cubic angstroms, and r in angstroms, interaction energies (E) in electronvolts for various metal−ligand combinations are calculated as follows:

one ligand:

$$E(M^{2+}-L) = \Delta - 6.0\mu/r^2 - 28.8\alpha/r^4 \qquad (1)$$

$$E(M^+-L^+) = 14.4/r - 3.0\mu/r^2 - 14.4\alpha/r^4 \qquad (2)$$

two ligands:

$$E(M^{2+}-L_2) = \Delta - 12.0\mu/r^2 - 57.6\alpha/r^4 \qquad (3)$$

$$E(M^+-L_2^+) = 14.4/r - 6.0\mu/r^2 - 21.6\alpha/r^4 \qquad (4)$$

The combination represented by eq 4 has a degeneracy which is associated with charge transfer between the ligands; this contribution is small, although one component of it will mix with the M^{2+} state. The most important consideration is that the long-range terms (electrostatic interactions) are based on charge-localized structures and not on configurations of the form $L^{1/2+}-M^+-L^{1/2+}$.

From these equations, two important distances are calculated. r_{stab} is the distance at which $E(M^{2+}-L)$ and $E(M^{2+}-L_2)$ are zero, and r_{cross} is the distance at which the energies represented by eqs 1 and 2 or eqs 3 and 4 become equal (the positions of the avoided crossings). These terms are illustrated in Figure 2, where they are placed in relation to a hard wall representing the repulsive interaction between the metal ion and the ligands. The exact position of the repulsive wall is unknown but can be estimated from a consideration of the results presented here. What is important for the stability of any $[M \cdot L_n]^{2+}$ combination is that the repulsive wall be located at a shorter M−L separation than r_{cross}; however, that may not be true of r_{stab}. Table 2 presents a summary of values calculated for r_{stab} and r_{cross} for Mg^{2+} in association with those ligands in Table 1 for which reliable data were available on all the necessary physical constants. Also shown is the effect of increasing the number of ligands from one to two. As the experimental data would suggest, the best

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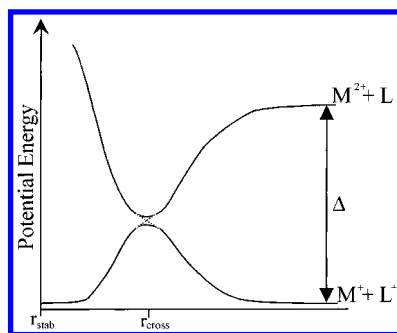
Figure 2. Schematic representation of the terms used in the application of an electrostatic model to discuss the stability of $[Mg(L)_n]^{2+}$ complexes.

Table 2. Calculated Curve Crossing Distances and Positions of the Potential Minima as a Function of the Number of Ligands Present in a $[Mg \cdot L_n]^{2+}$ Complex[a]

complex	one ligand		two ligands	
	r_{cross}/Å	r_{stab}/Å	r_{cross}/Å	r_{stab}/Å
$[Mg(CO_2)_n]^{2+}$	11.71	2.79	11.74	3.32
$[Mg(H_2O)_n]^{2+}$	6.31	2.64	6.67	3.46
$[Mg(CH_3CN)_n]^{2+}$	5.89	3.45	6.54	4.56
	7.97	**2.96**	**8.31**	**3.78**
$[Mg(C_4H_9NH_2)_n]^{2+}$	3.49	2.96	4.07	3.57
$[Mg(C_5H_{10}O)_n]^{2+}$	3.26	2.65	3.74	3.16
$[Mg(C_4H_5N)_n]^{2+}$	3.37	2.94	4.03	3.72
$[Mg(C_5H_5N)_n]^{2+}$	3.39	2.81	3.96	3.47
$[Mg(THF)_n]^{2+}$	3.32	2.75	3.87	3.36
$[Mg(\{CH_3CH_2\}_2O)_n]^{2+}$	3.34	2.71	3.86	3.21
$[Mg(C_4H_8O)_n]^{2+}$	3.51	2.85	4.10	3.56
	3.38	**2.81**	**3.94**	**3.43**
$[Mg(NH_3)_n]^{2+}$	3.39	2.19	3.76	2.73
$[Mg(CH_3OH)_n]^{2+}$	3.89	2.45	4.30	3.08
$[Mg(C_2H_5OH)_n]^{2+}$	3.76	2.64	4.24	3.27
$[Mg(C_3H_7OH)_n]^{2+}$	3.64	2.71	4.14	3.32
$[Mg(\{CH_3\}_2CO)_n]^{2+}$	3.53	2.76	4.11	3.47
$[Mg(penta\ 2,4\ dione)_n]^{2+}$	3.11	2.63	3.61	3.13
	3.55	**2.56**	**4.02**	**3.16**
$[Mg(NO)_n]^{2+}$	2.72	1.72	2.95	2.06

[a] Values in bold represent averages of the results given for the group of ligands immediately above. The ligands are grouped according to the physical properties identified in Table 1.

candidates for stabilizing the metal ion are those ligands with high ionization energies, which result in Δ having comparatively small values and places the crossing points at large metal–ligand distances. Thus, two waters in close proximity to Mg^{2+} are sufficient to confer electronic stability to the unit. The success of water in this context is clearly of considerable significance in biological systems and would account for the ubiquity of the ligand in the stabilization and coordination of Mg^{2+} in protein and nucleotide binding sites.[24] A further aspect of the calculations is the observation that the potential minimum for water is located at a comparatively long distance. Although the calculations are only semiquantitative, this result would agree with some observations regarding metal–ligand distances determined from crystallographic studies.[24]

The one other potential ligand that falls within the same category as water is acetonitrile, which has a much larger dipole moment, and the effect of this is to shift the potential minimum to a distance even larger than that seen for water. Primarily because of its high ionization energy, CO_2 is predicted to be as effective at stabilizing Mg^{2+} as the other ligands in this category.

For the second group of ligands, where the polarizabilities are high but the IEs are low, it can be seen from Table 2 that there has been a considerable decrease in the position of the
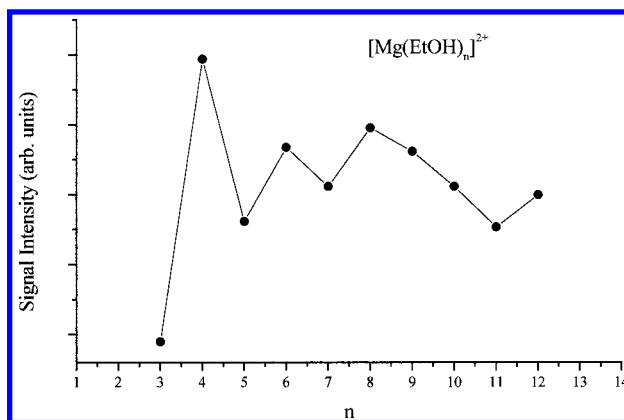

Figure 3. Relative intensities of $[Mg(C_2H_5OH)_n]^{2+}$ complexes plotted as a function of n.

crossing point when compared with those of the high IE ligands. However, the distances are still well outside of those considered appropriate for the bond lengths found in stable $Mg^{2+}-L$ compounds.[24,36] This is also true of the final group, which appears to be stable because they combine a higher IE with a modest dipole and polarizability. On average, ligands falling within the latter group require three molecules to stabilize Mg^{2+} with respect to charge transfer. From Table 2, it can be seen that the trends in r_{stab} and r_{cross} are such that, with the presence of three ligands, both these quantities will be larger than those determined for the ligands with high polarizabilities.

It is quite clear from the trends discussed above that the $[Mg(NO_n)]^{2+}$ system is unstable because the position of the charge-transfer crossing point is almost 1 Å closer to the metal ion than for any of the other ligands. Although the IE of NO is no lower than those of some of the other ligands discussed above, this is combined with a small dipole moment and low polarizability. However, the most obvious anomaly is in Table 1 is DMSO. Based on the dipole moment and polarizability data, this molecule should form a stable complex with Mg^{2+}. Kebarle and co-workers[30,31] have reported results on the formation of stable gas-phase complexes of Cu^{2+} and La^{3+} with DMSO, but to our knowledge no electrospray data have been presented on DMSO in association with doubly charged alkaline earth metals. Since there are no obvious physical reasons why DMSO should not bind to Mg^{2+}, it is quite possible that the lack of $[Mg(DMSO)_n]^{2+}$ complexes from the 'pick-up' experiments identifies a flaw in the technique.

Individual Systems. (1) Hydrogen-Bonded Solvents: H_2O, CH_3OH, and CH_3CH_2OH. The intensity distribution recorded for $[Mg(CH_3CH_2OH)_n]^{2+}$ as a function of n is shown in Figure 3. The profile is characteristic of all three ligands and is thought to be strongly influenced by hydrogen bonding. The primary solvation shell is rigidly bound to the metal by ion–dipole and induced dipole interactions. Additional molecules, which form a secondary solvation shell, are then held in position by the primary shell through the presence of charge-enhanced hydrogen bonds.[11] In some instances, this pattern of behavior is thought to extend into the tertiary solvation shell.[39,64] These extended units could be viewed as model outer-sphere coordination complexes and have been shown to be associated with the hydrolysis reaction that leads to the formation of Mg^+OH.[64,65] Characteristic of a network of hydrogen bonds are the observa-

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(65) Beyer, M.; William, E. R.; Bondybey, V. E. *J. Am. Chem. Soc.* **1999**, *121*, 1565.

tion of a very gradual decline in cluster ion intensity as a function of size[39,64,66] and the presence of intensity plateaus extending out to complexes containing up to 20 solvent molecules.[39,66] There is, however, a limitation to the influence of hydrogen bonding, and this appears to be primarily determined by size. For alcohol molecules larger than ethanol, their distributions of relative intensity decline very rapidly beyond what are assumed to be their primary coordination numbers. For example, for propanol the distribution of $[Mg(C_3H_7OH)_n]^{2+}$ ions reaches a peak at $n = 4$, and then declines rapidly such that at $n = 10$ the ion intensity is just 8% of the maximum.[67] This behavior is in marked contrast to that shown in Figure 3. To form a stable network of hydrogen bonds, molecules in the second solvation shell require access to the hydroxyl hydrogen atoms of those molecules in the primary shell. However, as the complexity of the hydrocarbon component increases, that requirement will become increasingly more difficult to achieve.

Note that, although ammonia and related amines are capable of hydrogen bonding, there is no evidence from the experimental data that these molecules in association with Mg^{2+} form the type of extended hydrogen bond network seen for water and the smaller alcohol molecules. This observation could have important implications for the role of amines in the formation of outer-sphere complexes with Mg^{2+}. The results are, however, in marked contrast to data recorded for Cu(II), where water and ammonia were observed to behave in a very similar fashion;[48,49] these results have recently been interpreted using density functional theory.[68]

Data resulting from MIKE scans on Mg^{2+} complexes with water and methanol have been presented elsewhere.[39,64] With water it was possible to identify two separate charge-transfer routes in the smaller clusters.[64] In association with methanol, Mg^{2+} has been found to promote a wide range of chemical processes, many involving charge transfer.[39]

(2) Aprotic Solvents: Acetone, Pyridine, and Acetonitrile. Typical examples of intensity profiles recorded for ligands of this type as a function of cluster size are shown in Figure 4, and similar data on THF have been presented in an earlier publication.[53] The (assumed) most stable ion contains four ligands, and the intensities of larger species decline rapidly beyond that size. These observations are consistent with the general view that organomagnesium compounds adopt tetrahedral geometry,[36] a pattern of behavior that contrasts markedly with that seen in systems where the ligands are capable of forming hydrogen bonds, cf. Figure 3. In the case of THF, the four-fold coordination coincides with structural data on a range of stable solid-state complexes which contain the unit $[Mg(THF)_4]^{2+}$ in association with various counterions.[36] In view of their size and very specific level of coordination, these ligands could be viewed as better models for the picture of a distinct first solvation shell, than, for example, water.

Figure 5 shows two examples of MIKE spectra recorded following the collisional activation of $[^{25}Mg(2\text{-butanone})_4]^{2+}$ (a) and $[^{25}Mg(\text{pyridine})_4]^{2+}$ (b). Both show evidence of unimolecular fragmentation, with the loss of one and two neutral ligands being very prominent. In addition, there are broader features due to charge transfer followed by Coulomb explosion of each of the complexes. In comparison to the analogous copper(II), silver(II), and gold(II) complexes,[50,51,54] these data differ in one respect: apart from the slightly higher intensity of the Mg^+L fragment, there appears to be no strong preference
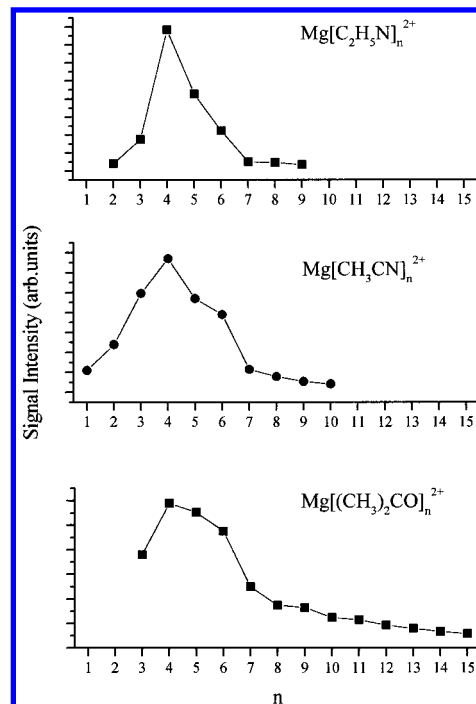
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Figure 4. Relative intensities of complexes formed from aprotic solvents in association with Mg^{2+} plotted as a function of n: (a) $[Mg(C_5H_5N)_n]^{2+}$, (b) $[Mg(CH_3CN)_n]^{2+}$, (c) $[Mg(\{CH_3\}_2CO)_n]^{2+}$.
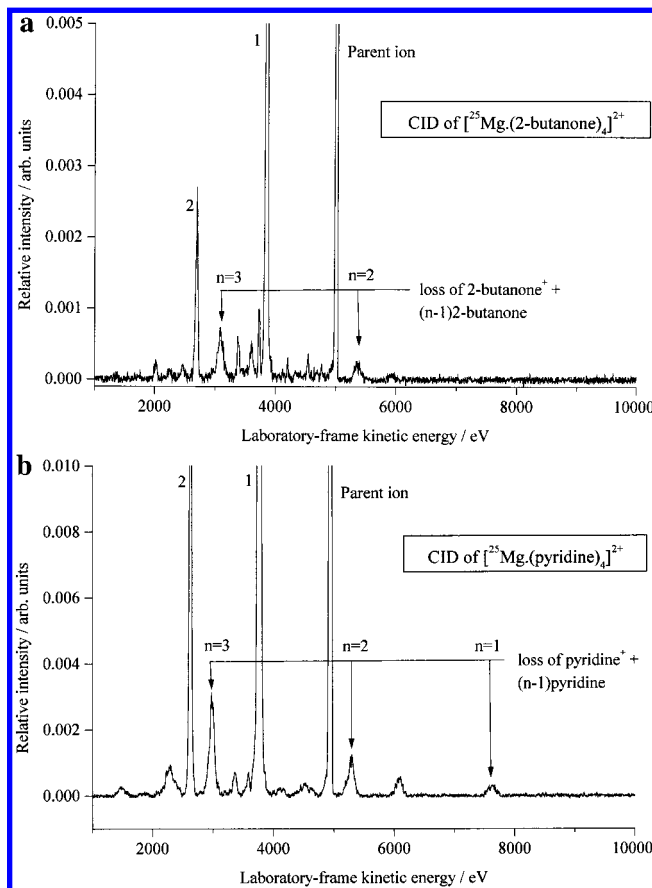

Figure 5. Ion kinetic energy (MIKE) spectra recorded following the collisional activation of (a) $[^{25}Mg(2\text{-butanone})_4]^{2+}$ and (b) $[^{25}Mg(\text{pyridine})_4]^{2+}$. The peaks denoted by 1 and 2 correspond to the loss of one and two neutral molecules, respectively, from the parent ion.

for a particular charge-transfer process. In contrast, M^+L_2 fragments dominate the equivalent spectra for Cu(II) and Au-(II),[51] a factor that reflects the stability of the M^+L_2 unit in the

condensed phase.[19] Many of the MIKE spectra recorded for other ligands given in Table 1 are qualitatively similar to those given either in Figure 5 or in other publications. The single most common aspect to all the data is that the probability of charge transfer declines very rapidly beyond the first solvation shell; thus, the fragmentation patterns of most $[Mg(L)_6]^{2+}$ complexes are dominated by the loss of neutral ligands.

(3) Bidentate Ligands: Penta-2,4-dione and Ethylenediamine. Only one of the bidentate ligands proved successful at forming a stable, doubly charged complex. Failure to observe a stable unit with the diamine is not too surprising; the molecule has a very low IE, which means that each attachment would have to stabilize the complex to a very high degree. Given that up to two ligands might be expected to attach themselves, then each would have to contribute to the complex a stabilization energy of 3.5 eV. In the case of penta-2,4-dione, we are clearly unable to tell from the data available whether both points of contact within each molecule are, indeed, attached to Mg^{2+}. However, on the basis of the analysis of unidentate ligands given above, it can be seen that those with ionization energies and polarizabilities comparable to those of penta-2,4-dione all require attachment at two sites to stabilize the ion. This observation, together with the fact that the ion with maximum intensity contains two penta-2,4-dione molecules, does suggest bidentate behavior. This being the case, then the complex would match the four-fold coordination seen with 13 of the other (unidentate) ligands and would also be consistent with the coordination of many solid-state Mg^{2+} complexes.[36] There is a counter-argument to be made against bidentate behavior: if one end of a ligand becomes attached, then the probability of a second attachment is probably going to be quite low. The reasons for this are, first, entropy and, second, that the positive charge on the metal will polarize the electrons on the ligand, leading to a charge of $\delta+$ appearing at the unattached end, which will be repelled as it approaches the metal ion. A contributing factor will be the absence of p and d electrons on the metal, as these not only would have provided directional bonding but also would shield the $\delta+$ charge from the strong positive charge on the ion core. The observation of a complex with penta-2,4-dione is, we believe, the first recorded example of bidentate Mg^{2+} coordination in the gas phase.

Conclusion

Using a wide variety of ligands, it has been shown that the ability of a solvent to stabilize Mg(II) can be understood at a semiquantitative level in terms of the physical properties of the molecules concerned. As an example, the results show that the high ionization energy of water is primarily responsible for the molecule's remarkable ability to stabilize Mg(II). The model calculations also suggest that the influence of a molecule may be effective over comparatively long distances, which could fit with structural observations on biological systems.[24] Equally interesting is the ability of CO_2 to stabilize Mg(II), again as a direct consequence of the molecule's high ionization energy. Although not of direct biological relevance, where such a strong interaction between CO_2 and Mg(II) may be of significance is in the fixation of carbon dioxide within chloroplasts.[69] Given that Mg(II) is classified as a "hard" Lewis acid,[23] then the ligands deemed to be most successful in these experiments might be considered as "hard" Lewis bases.[23] However, within that classification, these results provide an opportunity to "fine-tune" the "hardness" of the base scale with respect to Mg^{2+} as follows: $H_2O \approx RCN \approx CO_2 > RNH_2 \approx R_2O > NH_3 \approx ROH \approx R_2CO$.

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