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Stable Ag(II) Coordination Complexes in the Gas Phase

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Abstract: The preparation and study of gas-phase transition-metal complexes in their higher oxidation states, i.e., Cu(II), Cr(III), Fe(II), etc., presents a considerable technical challenge. Charge transfer prevents such species from being “grown” as cluster ions and techniques, such as electrospray, do not always produce the desired charge state or allow for experiments to be performed on a broad range of ligands. Discussed here are new results from a technique which promises to overcome some of these problems, and appears capable of producing complexes from a wide variety of metals and ligands. Data are presented for complexes based on silver(II) in association with a broad range of ligands, including pyridine, tetrahydrofuran, and benzene. For each $[\text{AgL}_n]^{2+}$ system, two important quantities are identified: (i) the minimum number of ligands required to form a stable unit and (ii) the value of n for which the intensity distribution reaches a maximum. For nitrogen-containing ligands these numbers are 2 and 4, respectively, and for oxygen-containing ligands 4 and 5. A series of aromatic ligands all exhibit coordination numbers of 2. For several of the nitrogen-based ligands the most stable combinations correspond to those identified in the condensed phase, and $[\text{Ag}(\text{pyridine})_4]^{2+}$ is a very good example of such behavior. In the case of the oxygen-containing ligands, there are no direct condensed-phase analogues, but some of the more stable combinations identified may offer prospects for future preparative work. Within the latter group, not only was the presence of stable silver(II)/CO₂ complexes very unexpected, but with $[\text{Ag}(\text{CO}_2)_4]^{2+}$ being the most stable combination, the pattern of behavior is markedly different from that of other oxygen-containing ligands. The composition and charge states of many of the stable complexes were confirmed via collisional activation, where both ligand loss and charge-transfer processes could be identified. Only one example of a chemical reaction could be clearly identified as being initiated by the presence of silver(II).

Introduction

To date, most experimental studies of metal ion coordination in the gas phase have been restricted to singly charged species,^{1,2} a situation that contrasts markedly with the fact that many of the more important metal ions in condensed-phase chemistry and biochemistry are multiply charged.^{3,4} Unlike singly charged ions, multiply charged metal ions in solution are frequently expressed in the form of a solvent complex, for example, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ni}(\text{NH}_3)_6]^{2+}$,³ where this notation acknowledges an implicit relationship between an ion and the bulk solvent. Since an isolated multiply charged ion, for example, Cu^{2+} , cannot coexist in the presence of a single monodentate solvent molecule, the solvent complex terminology is particularly appropriate. The circumstances responsible for this situation can easily be explained through a consideration of the second ionization energy (IE) of a typical transition metal and the first IE of an organic solvent. The subject matter of this paper, Ag(II), is a particularly good illustration, because silver has the highest second ionization energy (21.5 eV) of the transition metals. Therefore, it should be the most difficult metal ion to stabilize in the form of a gas-phase doubly charged complex with ligands which may have typical IEs of ~11 eV. On the

basis of just a simple consideration of the energy difference between Ag(II) and an organic ligand, it is apparent that charge transfer should be spontaneous whenever the ion and a few solvent molecules come into contact. However, the large stabilization energy required to form a silver(II) complex is not just a gas-phase phenomenon. Such compounds are also difficult to prepare in the condensed state because Ag(II) acts as a powerful oxidizing (charge-transfer) agent and only a very select group of organic ligands is capable of stabilizing the ion, often in the presence of a nonreducing acid. The fact that such complexes can be formed serves to illustrate that the stability of a multiply charged metal ion (with respect to reduction) is intimately coupled to the properties of the ligand (solvent) in a way that is not necessarily true for singly charged metal ions. This statement is particularly true for complexes formed in the gas phase, where charge transfer between a singly charged metal ion and a ligand is a very unusual event.

From the viewpoint of gas-phase clusters of the form $[\text{AgL}_n]^{2+}$, it is probably appropriate to consider those interactions that are responsible for their stability, and how these may influence what is observed as a function of cluster size and composition. As part of the experimental program discussed below, we shall examine both the unimolecular loss of single ligands and collision-induced charge transfer, in which the metal ion changes oxidation state from Ag^{2+} to Ag^+ .

The interaction between a single neutral ligand and a doubly charged metal ion can be summarized graphically as shown in Figure 1a, where a model due primarily to Tonkyn and

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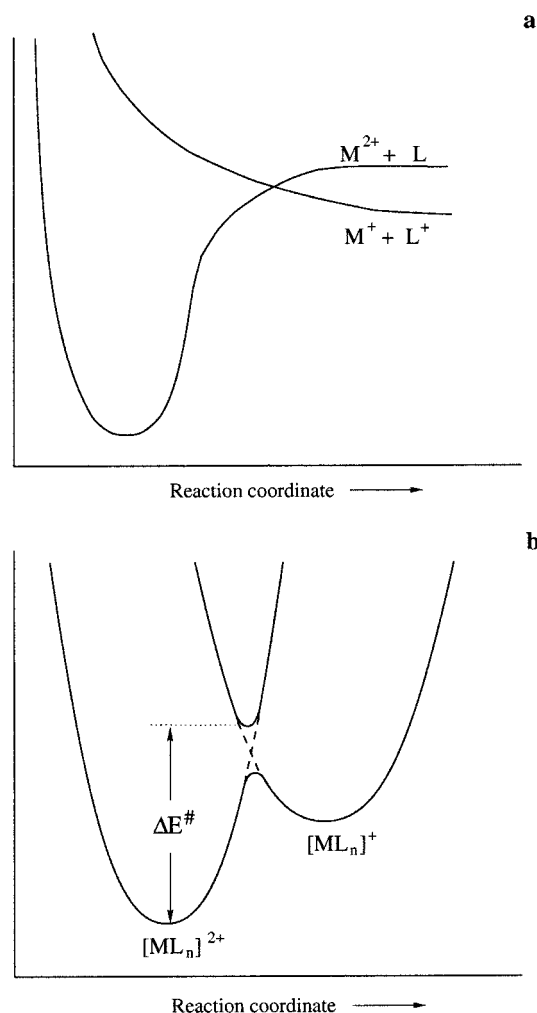


Figure 1. Schematic diagrams representing the interaction between a multiply charged metal ion and a variable number of ligands: (a) in the gas phase where direct charge transfer can occur between the metal ion and a single ligand (L) (adapted from ref 11); (b) in a cluster containing several ligands and/or in a solution of L ; ΔE^\ddagger represents a barrier to charge transfer; further details are given in the text (adapted from ref 12).

Weisshaar⁵ has been adapted to suit these particular circumstances. The ligand is attracted to the ion via a strong induced dipole interaction, $V(r) = -\alpha q^2/r^4$, where α is the polarizability of the ligand concerned, $q = +2$ (the charge on the ion), and r is the separation between the ligand and the ion. Also shown is a second curve which represents the purely repulsive Coulomb interaction that would result from charge transfer, and this potential is given by $V(r) = +q^2/r$. At infinite separation, potential energy differences between the two interactions are determined by the value of $IE(\text{Ag}^+) - IE(L)$. If this number is large, then charge transfer can be accompanied by a large release of kinetic energy, and examples of such behavior in small $[\text{Mg}(\text{ROH})_n]^{2+}$ clusters have been presented previously.⁶ Further examples of kinetic energy release measurements following charge transfer in multiply charged complexes can be found in refs 7 and 8. The high exothermicity associated with the process described in Figure 1a also serves to explain why it is difficult

to prepare doubly charged metal complexes containing a single ligand molecule. A theoretical analysis of stable doubly charged metal nitrides of the form $M^{2+}N$ can be found in a recent review by Harrison and Kunze,⁹ and Freiser et al.¹⁰ have observed stable doubly charged metal/hydrocarbon complexes, but usually in association with metals which have second IEs of ~ 12 eV.

In their analysis of competing reactions between doubly charged metal ions and alkanes, Weisshaar and co-workers arrived at a series of interaction boundaries within which certain processes were most likely to be observed.^{5,11} From their analysis, these authors concluded that when alkane molecules were at a critical distance of ~ 7 Å from the metal ion, there was a high probability of charge transfer. Other reactions, such as hydride transfer, were calculated to have different critical distances.⁵ A key factor in all these calculations is the reaction exothermicity, since this determines where curve crossing takes place between the (fixed) attractive potential and the various repulsive potential curves. Subtle differences in exothermicity explain why charge and hydride transfers have different critical distances.⁵

With regard to doubly charged complexes containing a number of ligands or solvent molecules, the situation for charge transfer will be significantly different from that above. It cannot simply be a question of shifting the curves shown in Figure 1a to allow for the differential solvation of M^{2+} and M^+ ; although solvation enthalpy changes may be in the order $M^{2+} > M^+$, the potential energy surfaces must cross at some point (or along a seam) because the energies of the isolated ions together with the solvent follow the pattern $M^{2+} < M^+$. As Marcus¹² has noted in an analysis of electron transfer in condensed-phase transition-metal complexes, the assignment of a reaction coordinate is no longer as obvious as that shown in Figure 1a. Several factors within the complex are influenced by the movement of a charge: (i) there will be small changes in ligand–metal distances because polarization interactions will be influenced by the reduction in charge density at the metal site; (ii) some of the ligand molecules may reorientate; (iii) the ligand accepting the charge will adopt a position with respect to the metal ion, which is different from the other “spectator” ligands. The net result is a many-dimensional surface, which at its simplest can be represented by Figure 1b.¹² Here, the passage from stable $[ML_m]^{2+}$ to stable $[ML_m]^+$ (where $m < n$) is presented in the form of two intersecting potential energy curves, which contain an avoided crossing, and charge transfer follows the lowest-energy adiabatic surface. Presented in this form, the surface contains an essential element which accounts for the stability of the doubly charged complexes observed in these experiments, namely, a barrier to charge transfer (ΔE^\ddagger) which as shown below can be overcome by collisional activation of the complexes. The relative depths of the two attractive wells (and hence the magnitude of the barrier) will shift as a function of the degree of solvation. For the observation of $[ML_n]^{2+}$ as a stable gas-phase complex, ΔE^\ddagger has to be greater than the internal energy received as a result of the preparative technique (see below). A second component to the multidimensional surface, which is not represented in Figure 1b, is the repulsive interaction that exists between $[ML_m]^+$ and L^+ (together with $[n-m-1]L$) once

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charge transfer has occurred. This surface should be similar to that in Figure 1a, but with M^{2+} and M^+ shifted by solvation.

The discussion above assumes that a significant fraction of the total charge resides on the central metal atom. However, there is a further important class of doubly charged ion, where the total positive charge is delocalized.¹³ Such behavior is typical of diatomic ions, such as He_2^{2+} and N_2^{2+} , where the covalent bond between the two singly charged atoms is strong enough to withstand the repulsive Coulomb interaction. Other examples of small multiply charged ions can be found in a review by Echt and Mark,¹³ and a quantitative rationale for their stability has been given by Gill and Radom.¹⁴ Although examples of these particular types of ions have been identified in silver(II) and copper(II) complexes, they will be the subject of a separate publication.¹⁵ In all of the examples discussed here, a major fraction of the double charge is believed to reside on the metal ion.

We have recently reported a new approach to generating multiply charged metal-containing clusters in the gas phase,^{6,16–19} and results have been presented for complexes of Cu(II), Mg(II), and Sr(II). In at least one case, $[Mg(thf)_4]^{2+}$, it was observed that the most stable metal/ligand configuration is analogous to the ionic core of a solid-state complex.¹⁶ The experiments have also provided an opportunity to explore the effects of ligands that are not commonly used in transition metal chemistry, e.g., acetone.¹⁹ Presented here are new results where a series of quite diverse ligands has been examined in an attempt to form stable gas-phase complexes with Ag(II). As noted above, silver has the highest second ionization energy of any metal; hence, many of the ligands failed to stabilize the ion. However, 10 Ag(II) complexes have been observed and characterized in terms of their most stable configurations, many of which conform to expectations in terms of coordination number. Several of the complexes, such as $[Ag(pyridine)_4]^{2+}$, have solid-state analogues, whereas others have not been observed in the bulk, but their identification here may offer opportunities for future preparative work in the condensed phase.

Experimental Section

The experiments detailed here utilize a commercial Knudsen effusion cell in conjunction with a VG ZAB-E double-focusing reverse geometry mass spectrometer. An extensive description of the general system of instrumentation used for generation, resolution, and detection of the cluster beam has been provided in previous work.²⁰ Of particular importance to this work is the use of a "pickup" technique by which mixed cluster neutrals consisting of silver and ligand molecules are produced. This enables the production of $[AgL_n]^{2+}$ within the ion source, where L is a solvating molecule.

A mixture of argon as a carrier gas and a solvent undergoes supersonic expansion through a pulsed conical nozzle. For ammonia, carbon dioxide, nitrogen dioxide, nitric oxide, and ethene, high-pressure cylinders containing 99% Ar and 1% solvent were used to produce the requisite mixture of gases. For the remainder of solvents studied in these experiments, argon was passed through a reservoir where the

solvents were held in their liquid state. This enabled solvent vapor to enter the argon stream, providing the gas mix necessary for the experiments. For solvents with relatively high vapor pressures, the reservoir was cooled in ice, enabling stable signals to be attained from each solvent over an extended period of time. A carrier gas backing pressure of approximately 45 psi was used in most experiments, and previous work has shown the use of argon to be crucial to the success of the pickup technique.²¹

The resultant cluster beam was collimated using a 1 mm diameter skimmer before passing through a region containing silver vapor produced from a Knudsen effusion cell operating at 1150 °C. This and previous work^{18,19} suggest the optimum partial pressure range for the production of mixed solvent/metal clusters to be between 10^{-1} and 10^{-2} Torr. At higher partial pressures there is destruction of the cluster beam due to scattering, and at lower partial pressures insufficient quantities of metal are picked up. A shutter at the exit of the effusion cell is used to confirm the presence of silver in the clusters. Where a survey is performed of the relative intensities of parent ions of a given series, the difference is taken between the signal intensity with the shutter open and closed. This approach removes any contribution from background ions that is not dependent on material originating from the effusion cell.

The cluster beam undergoes ionization by 100 eV electron impact approximately 70 cm downstream from the skimmer, and the resultant ions are accelerated with a potential of 5 kV. The beam passes through a field-free region before parent ion selection takes place according to the mass/charge ratio, within the magnetic sector of the instrument. Doubly charged species are transmitted through the magnetic sector at fields which also transmit singly charged species of half their mass. Hence, when referenced to the mass increment separating singly charged ions, doubly charged species appear in mass spectra at half-integer intervals.

A second field-free region (FFR) separates the magnetic sector from the electrostatic analyzer (ESA). The presence of a gas cell in this FFR makes it possible to study the collision-induced dissociation (CID) of size-selected parent cluster ions, and for many of the stable complexes, fragmentation processes were examined in the presence of $\sim 10^{-6}$ mbar of air as the collision gas. The fragments arising from CID processes were identified by scanning the ESA. Mass-analyzed ion kinetic energy (MIKE) scans were performed with the ion source operating at a potential of 5 kV, which allows the transmission of ions with kinetic energies of ≤ 10 keV.²² Two types of processes can be observed in the MIKE scans: unimolecular fragmentation of the parent ion by the loss of individual neutral ligand molecules, and singly charged ions produced by collision-induced charge transfer and followed by Coulomb explosion. These two processes can easily be distinguished because the latter is normally accompanied by a high release of center-of-mass kinetic energy, and at an ion source potential of 5 kV, they are the only ion fragments to be found at laboratory-frame kinetic energies of between 5 and 10 keV.²² If it is assumed that there is no energy loss during collisional excitation, then a singly charged ion created by charge transfer from a doubly charged ion will have twice the kinetic energy of a normal singly charged ion. Final ion detection takes place after the ESA using a Daly scintillation detector, where photon counting methods can be used to detect weak signals. Although the center of mass collision energies are quite high, fragment ions generated via the collisional ionization of ligands are not expected to contribute to the observed fragmentation patterns.

Estimated signal intensities are on the order of 10^{-11} A for the strongest ion signals. For this reason, the resolution of the mass spectrometer ($m/\Delta m$) was fixed at approximately 2000, which represents a compromise between the ability to identify high mass ions and having sufficient signal intensity to perform quantitative measurements on ion signal strengths. The fact that all measurements reproduced the silver isotope ratio leads us to believe that a significant fraction of the results reported here on ion intensities are not influenced by the presence of underlying ionic species with the same nominal masses.

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Table 1. Dipole Moment (μ), Polarizability (α), Proton Affinity (PA), and Ionization Energy (IE) of All the Solvents Tried as Ligands for Doubly Charged Silver Complexes^a

ligand	μ (D)	α (\AA^3)	PA (kJ/mol)	IE (eV)	n_{max}	n_{low}
pyridine (C ₅ H ₅ N)	2.21	9.18	924	9.25	4	2
acetonitrile (C ₂ H ₃ N)	3.92	4.40	788	12.19	4	2
acrylonitrile (C ₃ H ₃ N)	3.87	8.05	794	10.91	4	4
pyrazine (C ₄ H ₄ N ₂)	0	9.27		8.64	4	2
carbon dioxide (CO ₂)	0	2.91	548	13.77	4	2
acetone (C ₃ H ₆ O)	2.88	6.39	823	9.70	5	4
2-butanone (C ₄ H ₈ O)	2.78	8.13	836	9.51	5	4
tetrahydrofuran (C ₄ H ₈ O)	1.75		831	9.41	5	4
benzene (C ₆ H ₆)	0	10.32	759	9.25	2	2
benzonitrile (C ₇ H ₅ N)	4.18	12.5		9.62	2	2
water (H ₂ O)	1.85	1.45	689	12.61		
methanol (CH ₄ O)	1.70	3.29	761	10.85		
2-pentanone (C ₅ H ₁₀ O)		9.93	841	9.38		
2,4-pentanedione (C ₅ H ₈ O ₂)		10.5		8.85		
ammonia (NH ₃)	1.47	2.26	853	10.16		
pyrrole (C ₄ H ₅ N)	1.74		868	8.21		
ethylenediamine (C ₂ H ₈ N ₂)	1.99	7.2	945	8.6		
ethylene (C ₂ H ₄)	0	4.25	680	10.51		
nitric oxide (NO)	0.16	1.70	531	9.26		
nitrogen dioxide (NO ₂)	0.32	3.02		9.75		
dioxane (C ₄ H ₈ O ₂)	2.06	10.0	811	9.8		

^a Values taken from the *CRC Handbook of Chemistry and Physics*, 77th ed., 1996–97). The last two columns contain the number of molecules of the most stable complex for each ligand (n_{max}) and the minimum number of molecules attached (n_{low}).

Results

Given below is a general account of experiments with doubly charged complexes between silver and a variety of solvent molecules. Data from surveys of $[\text{AgL}_n]^{2+}$ parent ion intensities (as a function of n , where L is a solvating molecule or ligand) are presented, and their significance with reference to the stability of the complexes is discussed. Also presented are selected results from experiments into the collision-induced fragmentation of $[\text{AgL}_n]^{2+}$ complexes. Since there is some repetition in the pattern of behavior of the complexes following collisional activation, discussion is restricted to key examples. Of particular relevance in this study is production of gas-phase complexes of the form $[\text{Ag}(\text{pyridine})_n]^{2+}$, some of which have already been studied extensively in the condensed phase.²³ This section begins with a detailed analysis of the pyridine system, as a demonstration of the patterns of behavior displayed by these ions in the gas phase. For each of the other ligands, a short summary of observations is presented, together with a comprehensive list in Table 1 of all the solvents examined (stable and unstable ligand complexes). Also presented in Table 1 is a summary of some of the fundamental properties of the molecules concerned. For each solvent, two experimental measurements are listed in the table: n_{max} is the value for n at which the observed signal intensity of a silver(II) complex for a particular solvent is a maximum; n_{low} is the lowest value for n at which a stable complex is observed. The solvents which were found to complex with silver can be divided into three general categories: those where n_{max} is 2, 4, or 5.

Pyridine. A section of the mass spectrum recorded using pyridine (py) as a ligand is shown in Figure 2, where peaks corresponding to the doubly charged complexes $[\text{Ag}(\text{py})_4]^{2+}$ and $[\text{Ag}(\text{py})_5]^{2+}$ are indicated. The two peaks observed for each complex correspond to the two isotopes of silver (^{107}Ag and ^{109}Ag), and their intensities follow the natural abundance ratio of 52/48 ($^{107}\text{Ag}/^{109}\text{Ag}$). The mass spectrum is dominated by various singly charged ions, corresponding to the presence of

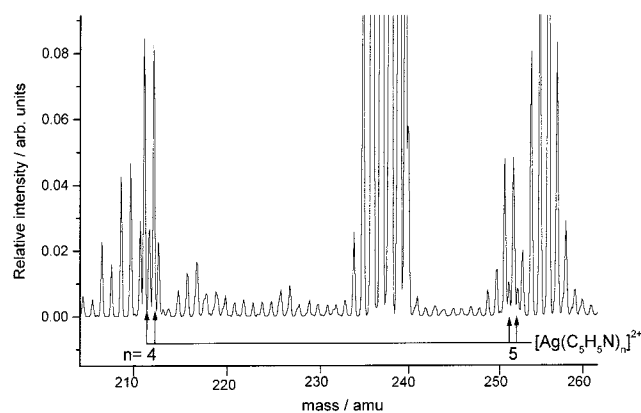


Figure 2. Section of a typical mass spectrum showing the presence of $[\text{Ag}(\text{pyridine})_n]^{2+}$ cluster ions for $n = 4$ and 5. Other features present arise from various combinations of pyridine and argon in the form of ionized clusters.

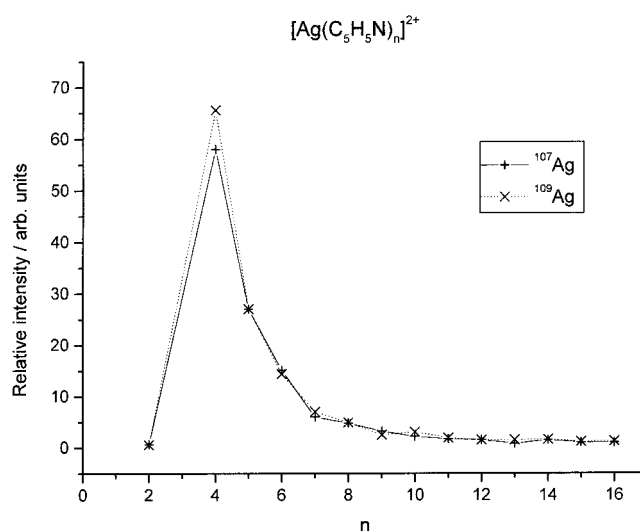


Figure 3. Relative intensities of $[\text{Ag}(\text{pyridine})_n]^{2+}$ cluster ions as a function of n . Data have been recorded for both the ^{107}Ag and ^{109}Ag isotopes of silver.

pyridine clusters, and mixed argon/pyridine clusters within the beam (a feature necessary for the success of the pickup process). Where the solvent has an odd nominal mass, such as pyridine, and n is also odd, doubly charged clusters are transmitted in coincidence with a singly charged ion of half the mass. Therefore, it was necessary to confirm the identities of peaks at odd values of n using the shutter on the effusion cell, and thus verify that signals arising from doubly charged pyridine/silver complexes were a significant proportion of each of the peaks. Such a procedure in the case of a mass coincidence is only possible when signals from the ions of interest are significantly more intense than those of any underlying singly charged ions. Figure 3 shows a plot of the relative intensities of the $[\text{Ag}(\text{py})_n]^{2+}$ complexes (for each silver isotope) as a function of n . The data show the presence of a sharp maximum at $n = 4$, followed by a rapid decrease in intensity as n increases. The signal eventually becomes constant for n in the range 8–16. It was not possible to resolve individual ion intensities for $n > 16$. Beyond the primary solvation shell, molecules will be retained by the ion through a combination of ion-induced dipole and van der Waals interactions. Since pyridine is highly polarizable, the former interaction can be expected to persist into the second solvation shell, which could contain between 12 and 20 molecules, and because all sites in this shell will be

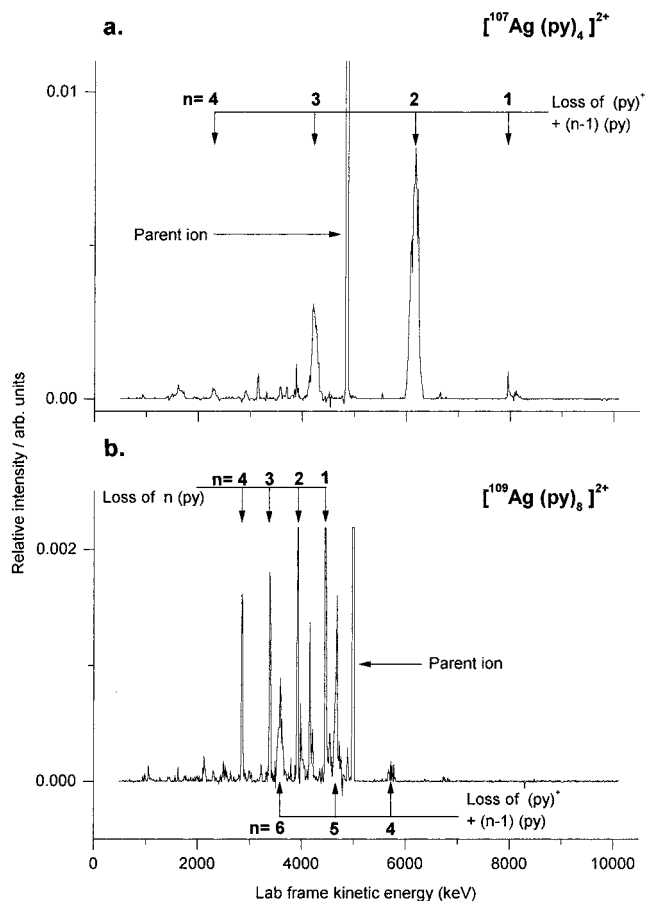


Figure 4. MIKE scans of size-selected $[\text{Ag}(\text{pyridine})_n]^{2+}$ cluster ions following collisional activation in the presence of air at $\sim 10^{-6}$ mbar, and with the ion source operating at a potential of 5 kV. Product ions arising from both the loss of neutral pyridine (unimolecular decay) and charge transfer are identified.

more or less equivalent, no discontinuities in intensity as a function of n are either expected or observed.

As stated in the Introduction, the $[\text{Ag}(\text{py})_4]^{2+}$ unit is one of the few silver(II) complexes to have been obtained^{23,24} in the condensed state in the presence of a nonreducing counterion, usually $[\text{S}_2\text{O}_8]^{2-}$. Thus, the observed maximum in Figure 2 at $n = 4$ for the gas-phase coordination of silver(II) by pyridine is in exact agreement with results previously obtained in the condensed phase. Of additional interest is the minimum number of ligand molecules required to stabilize the doubly charged silver ion, which in this case is found to be two. There is evidence of $[\text{Ag}(\text{py})_2]^{2+}$ having been detected in the condensed phase by EPR spectroscopy, but only in frozen nitric acid at 77 K.²⁵ The experimental results presented here would also suggest that the ion is comparatively stable, but as the CID data discussed below will show, the dimer complex is certainly more susceptible to reduction than $[\text{Ag}(\text{py})_4]^{2+}$.

Figure 4 contains the results of MIKE scans on the ions $^{107}\text{Ag}(\text{py})_4]^{2+}$ and $^{109}\text{Ag}(\text{py})_8]^{2+}$, and where fragment ions have been identified according to changes in the laboratory frame kinetic energy. The intense, narrow peaks seen at 5 keV correspond to the parent ions, and the broad peaks are produced as a result of collision-induced charge transfer followed by Coulomb explosion. The latter process has associated with it a significant release of kinetic energy, which is responsible for

the observed broadening of the peaks. As indicated in Figure 4a, collisional activation of the $^{107}\text{Ag}(\text{py})_4]^{2+}$ ion results in the loss of $\text{py}^+ + (n-1)\text{py}$, with $n = 1-4$ being observed. The peak corresponding to $n = 2$ is the most intense, which could imply that the preferred coordination geometry of the singly charged ion $\text{Ag}(\text{I})$ is 2. Although equilibrium thermodynamic data are available for gas-phase silver(I)/pyridine complexes, the experiments could only be performed on ions with three and four ligands.²⁶ Complementary data are available from the work of Deng and Kebarle²⁷ on $\text{Cu}(\text{I})$ with pyridine, and their results show the first two ligands to be very strongly bound to the metal ion. However, a contribution of importance comparable to that of the result in Figure 4a is the ease with which $^{107}\text{Ag}(\text{py})_2]^{2+}$ can be reduced in comparison, for example, to $[\text{Ag}(\text{py})_8]^{2+}$. In effect, the barrier shown in Figure 1b is very low, and the ion is only stable under very extreme conditions, i.e., unperturbed in the gas phase or in solid nitric acid at 77 K.²⁵

The CID scan recorded for the $^{109}\text{Ag}(\text{py})_8]^{2+}$ ion is shown in Figure 4b. Unlike the previous case, extensive loss of neutral ligands from the parent ion is observed in addition to charge-transfer-induced Coulomb explosion. Indicated in the figure are the losses of n py molecules, with n in the range 1–4. The sharp cutoff at $n = 4$ coincides with the observed stable complex $[\text{Ag}(\text{py})_4]^{2+}$. Charge-transfer peaks corresponding to the loss of $\text{py}^+ + (n-1)\text{py}$, with $n = 4-6$, are also seen in the MIKE scan. It can be seen that the complex has to drop in size to below $[\text{Ag}(\text{py})_4]^{2+}$ before charge transfer occurs; in effect, the collisional loss of ligands reduces the activation barrier shown in Figure 1b.

In the analysis of fragmentation patterns, such as those given in Figure 4, it is assumed, in the absence of any additional information, that charge transfer is accompanied by the loss of a singly charged ligand, L^+ . Many of the molecules investigated have high proton affinities (see Table 1), and in the presence of other gas-phase species are known to undergo a bimolecular ion–molecule reaction, leading to the formation of LH^+ . While it is quite conceivable that many of the products of charge transfer behave in a similar manner, the widths of the charge-transfer peaks prevent accurate mass assignment to within ± 1 amu. Only where there is unambiguous evidence of additional chemical reactivity is the possibility of ligand fragmentation discussed.

Complexes with Coordination Number $n_{\text{max}} = 5$. Acetone and 2-Butanone. Of the various silver/solvent complexes found where $n_{\text{max}} = 5$, the use of acetone as a ligand provided complexes with particularly high intensities. The results of a survey of the relative intensities of $[\text{Ag}(\text{ace})_n]^{2+}$ ions as a function of n are shown in Figure 5a, where a maximum at $n = 5$ can be seen, and the minimum number of acetone ligands required to stabilize the silver(II) ion is four. The collisional activation of $^{107}\text{Ag}(\text{ace})_5]^{2+}$ promoted the loss of a single neutral acetone molecule, and provided evidence of a charge-transfer process initiated by the loss of two molecules, which confirms the minimum stable size as $[\text{Ag}(\text{ace})_4]^{2+}$. A similar experiment on $^{107}\text{Ag}(\text{ace})_6]^{2+}$ revealed four charge-transfer channels, corresponding to the loss of between two and five acetone units, with the loss of four acetone molecules being the most intense. When $n = 7$, the most intense charge-transfer process corresponds to the loss of five acetone units, again leaving $[\text{Ag}(\text{ace})_2]^+$, and no charge transfer is observed when fewer than three molecules are lost from the parent ion.

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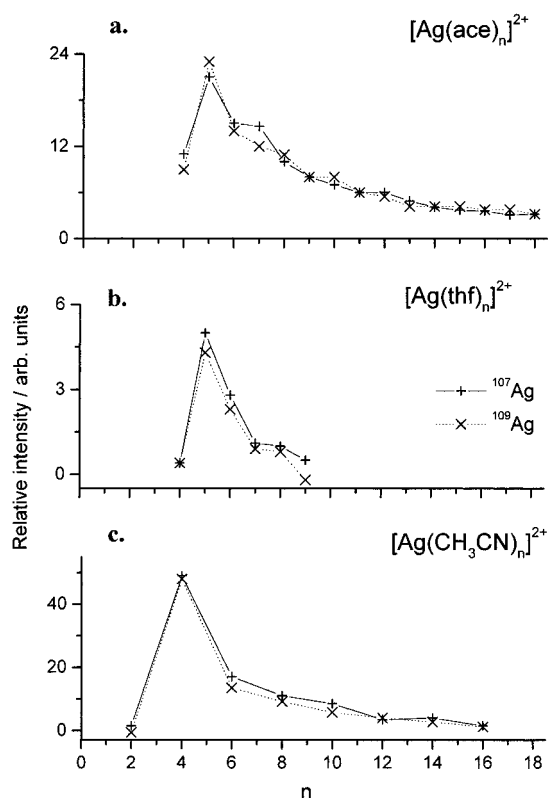


Figure 5. Series of plots showing the relative intensities of $[Ag(L)_n]^{2+}$ cluster ions as a function of n : (a) L = acetone; (b) L = tetrahydrofuran; (c) L = acetonitrile.

Experiments with 2-butanone also confirmed the presence of stable silver(II) complexes of the form $[Ag(C_4H_8O)_n]^{2+}$, with characteristics very similar to those recorded for the acetone system, namely $n_{\max} = 5$ and $n_{\min} = 4$. However, stable complexes were not observed for either 2-pentanone or 2,4-pentanedione as ligands. Both of these molecules should have electronic properties that are very similar to those of the two successful ketones discussed above. However, both ligands are significantly larger than 2-butanone; therefore, it is quite possible that steric factors prevent the coordination of a number sufficient to stabilize a silver(II) complex. This latter point is particularly relevant when considered in terms of the more general observation that silver(II) complexes with oxygen-containing ligands appear to require 5-fold coordination for stability. With reference to the fact that 2,4-pentanedione can act as a bidentate ligand, none of the metals studied thus far have shown any evidence of forming bidentate complexes in the gas phase using the pickup technique.

Tetrahydrofuran (thf). The patterns of behavior observed when thf is used as a ligand show several similarities to the results recorded for complexes containing acetone. A survey of parent ion intensities for $[Ag(thf)_n]^{2+}$ complexes as a function of n is shown in Figure 5b. Again, there is a maximum at $n = 5$, and the smallest observed stable complex occurs at $n = 4$. It was not possible to detect ions at values of n greater than 9, which contrasts with acetone where measurements were made on ions containing up to 18 molecules. However, the signal intensities of silver(II) complexes with thf (and 2-butanone) were much lower than those recorded for acetone, which obviously contributes to the likelihood of detection at high values of n . A MIKE/CID scan of $[^{107}Ag(thf)_5]^{2+}$ shows a pattern of behavior very similar to that seen for acetone, with the most intense charge-transfer channel arising from the loss of three thf units.

The only observed neutral loss is that of a single molecule, which in part confirms the minimum stable size as $[Ag(thf)_4]^{2+}$.

Complexes with Coordination Number $n_{\max} = 4$. Acetonitrile. In common with several other nitrogen-containing ligands examined in the present work, acetonitrile has an odd mass. Therefore, when n is odd, mass coincidences occur between doubly charged clusters of $[Ag(CH_3CN)_n]^{2+}$ and singly charged clusters of half the mass. The signal intensities from silver/acetonitrile complexes were strong enough to permit the acquisition of parent ion intensities (with odd n included), by taking the difference between the signals with the shutter open and closed. However, the data for odd-sized complexes are considered less reliable than those recorded for even-sized ions, and have therefore been omitted from the results shown in Figure 5c. A maximum in intensity is observed for $n = 4$, and complexes are observed at n as low as 2, and as high as 16 before the signals became too weak to record. Acetonitrile appears to be coordinating in the same way as pyridine, possibly as a consequence of there being strong electron-donating nitrogen groups in both ligands (see below). Taking the data presented in Figure 5 as a whole, the results provide a good illustration of the marked difference between nitrogen- and oxygen-containing ligands.

CID scans were performed on the $[^{107}Ag(CH_3CN)_n]^{2+}$ ions for $n = 4, 6$, and 8, and in every case the dominant charge-transfer step was that leading to the singly charged $[^{107}Ag(CH_3CN)_2]^+$ species, which would imply that this ion is particularly stable. However, this observation would also suggest that the barrier to charge transfer is quite high, certainly higher than that present in any of the ketone-containing complexes. The degree of neutral loss from each of the doubly charged complexes varies according to the size of the parent ion. Whereas for $n = 4$, the only neutral loss observed is that of a single CH_3CN , this number increases up to four molecules when $n = 8$. These data support evidence from the parent ion intensity survey, that $n = 4$ is the most stable complex. This observation is also consistent with the limited information available on solid-state complexes, where the stable cation is $[Ag(CH_3CN)_4]^{2+}$ and is understood to be planar.

Pyrazine (pyz). Similar to other nitrogen-containing ligands considered here, the intensity maximum occurs at $n = 4$, and the minimum number of molecules required to stabilize $Ag(II)$ is two. Both of these observations are significant in terms of comparisons with condensed-phase analogues. The minimum stable $[Ag(pyz)_2]^{2+}$ unit is equivalent to the crystalline $Ag(II)$ complex with pyrazine which takes the form $Ag(pyz)_2 \cdot S_2O_8$.²⁸ However, spectroscopic measurements on the latter indicate the presence of bridging pyrazine molecules in the form of a polymeric chain, in which each $Ag(II)$ experiences 4-fold coordination from additional pyrazine molecules on adjacent $[Ag(pyz)_2]^{2+}$ units.²⁸ This observation would account for the enhanced intensity of the $[Ag(pyz)_4]^{2+}$ complex. CID measurements on size-selected $[Ag(pyz)_n]^{2+}$ complexes show the presence of charge-transfer processes, but to be initiated these reactions require a reduction in size to $[Ag(pyz)_4]^{2+}$ or below.

Acrylonitrile (acr). Only one complex was observed between silver and acrylonitrile, and that corresponded to $[Ag(acr)_4]^{2+}$. The behavior of the ion following collisional activation was very similar to that seen for complexes containing acetonitrile.

Carbon Dioxide. Given the characteristics of those ligands discussed above, the appearance of stable silver(II) complexes with carbon dioxide as a ligand was quite unexpected. However, where the molecule gains over other ligands with small

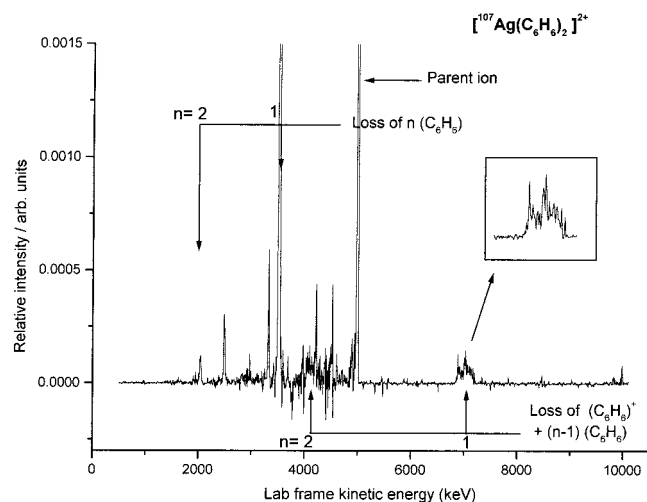


Figure 6. As for Figure 4, but for $[\text{Ag}(\text{C}_6\text{H}_6)_2]^{2+}$.

polarizabilities is that the ionization energy of CO_2 is comparatively high (see Table 1), which serves to reduce the energy deficit required to stabilize the metal ion. The results seen for carbon dioxide as a ligand do not follow the pattern seen for other oxygen-containing molecules in that the most intense (stable) combination corresponds to $[\text{Ag}(\text{CO}_2)_4]^{2+}$, and complexes are seen at values of n as low as 2. From Table 1, it can be seen that these characteristics are more typical of nitrogen-containing ligands.

CID studies were carried out on both $[\text{Ag}(\text{CO}_2)_4]^{2+}$ and $[\text{Ag}(\text{CO}_2)_6]^{2+}$. For $n = 4$, there are comparatively intense charge-transfer peaks following the loss of two and three molecules of CO_2 . However, as might be expected, the $n = 6$ complex is required to lose three or more molecules before charge transfer becomes a significant decay process. In addition, the ion also exhibits the loss of both one and two neutral carbon dioxide molecules as it fragments down to what is identified as the most stable structure, namely, $[\text{Ag}(\text{CO}_2)_4]^{2+}$.

These observations support the conclusion that the $[\text{Ag}(\text{CO}_2)_n]^{2+}$ series is stable because the carbon dioxide molecule successfully solvates silver(II), and that both charges remain on the metal once the complexes are formed. If this interpretation of the circumstances is correct, then it would suggest that silver(II) might be stable in supercritical CO_2 .^{29–31}

Complexes with Coordination Number $n_{\text{max}} = 2$. Benzene. Only one complex could be identified between silver(II) and benzene, and this corresponded to $[\text{Ag}(\text{C}_6\text{H}_6)_2]^{2+}$. The observation of an ion with this stoichiometry suggests that a sandwich configuration (where the centers of the two benzene rings are coaxial with the silver ion) may account for the stability of the ion (see below for further comment on this matter). Such a proposal would certainly be consistent with similar structures observed for other transition metals complexed with benzene in the condensed phase, e.g., $(\text{C}_6\text{H}_6)_2\text{Cr}^+$.³²

A CID scan of the $[\text{Ag}(\text{C}_6\text{H}_6)_2]^{2+}$ ion is shown in Figure 6, where it can be seen that charge transfer is accompanied by Coulomb explosion and the loss of one and two benzene molecules (with the loss of one molecule being more intense than two). The feature arising from the charge-transfer-induced

loss of one benzene is particularly broad and shows the presence of at least two peaks (see inset), which implies that these are contributions from more than one process. The mass difference between the two features corresponds to 2H_2 . Therefore, one possibility is that a chemical reaction accompanies Coulomb explosion, and that the loss of hydrogen together with C_6H_6^+ would allow the remaining radical to form a σ bond directly with silver(I).

It is interesting to note that there is a comparatively intense peak in Figure 6 corresponding to the neutral loss of one benzene molecule. This is unexpected, given that the complex $[\text{Ag}(\text{C}_6\text{H}_6)]^{2+}$ was not observed in the mass spectrum. However, the observation is made following collisional activation, which could mean that there is a substantial barrier to the loss of one molecule from the (assumed) very stable $[\text{Ag}(\text{C}_6\text{H}_6)_2]^{2+}$ unit, but that once formed, $[\text{Ag}(\text{C}_6\text{H}_6)]^{2+}$ is itself relatively unstable. A peak corresponding to the loss of two neutral molecules, while present, is far less intense.

In the literature, there are reports of Cu(II)/benzene complexes, but formed under conditions where they cannot be fully characterized.^{33,34} As far as silver is concerned, only Ag(I) has thus far been observed to form stable complexes with benzene in both the condensed³⁵ and gaseous^{36,37} phases.

Benzonitrile. As with benzene, benzonitrile was also observed to form only one complex, $[\text{Ag}(\text{C}_6\text{H}_5\text{CN})_2]^{2+}$. This suggests a pattern of behavior similar to that of benzene rather than of the other nitriles examined above. The two proposed sandwich structures $[\text{Ag}(\text{C}_6\text{H}_5\text{CN})_2]^{2+}$ and $[\text{Ag}(\text{C}_6\text{H}_5)_2]^{2+}$ certainly exhibit very similar behavior following collisional activation. The benzonitrile complex undergoes charge transfer accompanied by the loss one benzonitrile monomer, and the loss of two molecules is also present, but much less intense.

Discussion

Table 1 summarizes all the results from this series of experiments. The list of ligands contains not only those that were successful, but also all those that were tried but failed to yield quantitative information. The failure to observe a stable doubly charged ion may not necessarily be for reasons of ionic stability. The route to ion formation involves the initial formation of a neutral AgL_n species, and any lack of success with this step could be responsible for the absence of the corresponding $[\text{AgL}_m]^{2+}$ complex. For a number of reasons, the range of ligands covered is not as comprehensive as might be encountered in a typical inorganic text.^{3,32} For example, it has not yet been possible to study either sulfur- or phosphorus-containing ligands. However, there are distinct trends within the available data, and these may suggest molecular properties that contribute to the success of particular ligands. Similarly, there are major differences between silver(II) and copper(II), which again may provide an atomic picture of ion stabilization.³⁸

From the results summarized in Table 1, it is evident that the ligands identified as capable of forming stable complexes with Ag(II) fall into three groups. All the nitrogen-containing ligands form complexes where $n_{\text{max}} = 4$, which corresponds to the 4-fold coordination exhibited by many analogous condensed-phase Ag(II) compounds.^{23,28} Crystalline structures of the latter

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show the ligands as adopting a square planar configuration; however, the less restrictive environment provided by the gas phase may allow some structural relaxation if steric interactions are significant. For the other two groups of ligands identified here, there are no direct condensed-phase analogues. From Table 1 it can be seen that there is an important distinction between nitrogen and oxygen in that when ligands contain the latter atom (apart from CO₂) five molecules are required to maximize the intensities of stable Ag(II) complexes. Although there are no solid-state organosilver(II) complexes where oxygen alone is the coordinating atom, there are examples where nitrogen and oxygen coordinate together, and exhibit both 4- and 6-fold coordination.^{23,28} It is probable that these complexes are stable because the superior electron-donating properties of nitrogen counteract the higher electronegativity of oxygen. It is the latter property that probably inhibits the use, for example, of thf as a ligand in condensed-phase Ag(II) compounds. The final group of ligands consists of aromatic units (excluding pyridine and pyrazine) where the coordination number is 2, which is suggestive of a sandwich structure. Although stable Ag(I)/ethene complexes could be identified in the mass spectra, ethene did not appear to form a stable complex with Ag(II), which in turn probably excludes the possibility of [Ag(C₆H₆)₂]²⁺ being a π/σ donor/acceptor complex.

Listed for each of the ligands in Table 1 are a range of physical properties which may be associated with the ability of a molecule to form a stable complex. If a comparison is made between the oxygen-containing and nitrogen-containing complexes in terms of Lewis base structures, then the obvious preference for nitrogen to stabilize Ag(II) would suggest that the metal ion is "soft" (soft metals attract soft ligands).^{39–41} In addition, the expanded 4d orbitals make the metal ion receptive to ligands which will form covalent bonds. However, the situation is slightly more complicated than is suggested by a simple comparison of atomic sites with different degrees of electronegativity and orbital overlap. At a molecular level, electron donation from the ligand has to compensate for the large difference in ionization energies (typically ~12 eV), but it is not obvious from the properties listed in Table 1 what, if any, single molecular property characterizes that ability. Pyridine is clearly an excellent electron donor, and the molecule meets all the requirements necessary to form a stable dsp² square planar structure,²³ utilizing the 4d, 5s, and 5p orbitals. The high polarizability of pyridine would appear to reflect the electron-donating capability of the molecule; however, the accompanying high proton affinity could also categorize pyridine as a "hard" ligand.³⁹ In contrast, the corresponding properties for acetonitrile are quite different, and yet the resultant Ag(II) complexes have stabilities that are comparable to those seen for [Ag(pyridine)_n]²⁺. Where acetonitrile gains is in having a relatively high ionization energy, which means that the required stabiliza-

tion energy is reduced by ~3 eV per molecule. The same characteristics appear to be responsible for CO₂ forming stable complexes.

There is a marked contrast between those N-containing ligands that can stabilize Ag(II) and the two ligands listed in Table 1 which do not. Prominent in the latter group is ammonia, which as an sp³ hybrid would be a stronger (harder!) base than the successful N-containing ligands listed. However, compared with the latter group, NH₃ is also distinguished by its relatively low polarizability. The failure of pyrrole to form stable complexes with Ag(II) can be accounted for on both steric and electronic grounds since, unlike pyridine, the electron pair on the nitrogen atom in pyrrole forms an integral component of the π electron network of the ring.

In the case of O-containing ligands, the two ketones clearly satisfy the requirements of having a pair of nonconjugated electrons which allow the oxygen atom in each case to act as a donor to the metal ion. However, in terms of electron-donating capability, there is obviously a subtle distinction between tetrahydrofuran (thf), which forms a stable complex with Ag(II), and H₂O and methanol, both of which fail to stabilize the metal. The only marked difference seen in Table 1 between the three ligands is that thf has the largest proton affinity. All three ligands are effective at forming stable complexes with Cu(II).³⁸ A feature that further distinguishes thf from all the other successful N- and O-containing ligands in Table 1 is that it does not have a vacant π^* system into which the metal ion can back-donate electron density.

Finally, an overall measure of the superior electron-donating properties of the nitrogen atom compared with oxygen is to be seen from the values of n_{low} given in Table 1. These numbers represent the minimum number of ligands required to stabilize Ag(II). For N-containing ligands, two is the most frequent value, whereas for oxygen the minimum stable size typically contains four ligands.

Conclusions

It has successfully been demonstrated that the metal atom pickup technique can be used to generate stable, gas-phase metal/ligand complexes in oxidation states that are difficult to observe in the condensed phase. Where valid comparisons are possible, the most stable metal/ligand combinations, for example, [Ag(pyridine)₄]²⁺, are equivalent to those determined for the solid-state analogues. What these experiments have allowed is for an investigation of other stable, but as yet unseen, complexes, and of these [Ag(CO₂)_n]²⁺ is probably the most unexpected. As a qualitative conclusion, it would appear that those ligands which combine high ionization energy with high polarizability are the most successful at stabilizing Ag(II).

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