Coordination and Chemistry of Stable Cu(II) Complexes in the Gas Phase

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A technique has been developed that provides a solution to the very considerable technical problem of preparing gas-phase complexes from transition metals in their higher oxidation states, i.e., Cu(II), Cr(III), Fe(II), etc. Charge transfer prevents complexes, such as $[Cu{\cdot}(H_2O)_n]^{2+}$, from being prepared via nucleation about an ion core, and yet these ions are pivotal to an understanding of transition metal chemistry. Discussed here are new results from a technique that appears capable of producing complexes from a wide variety of metals and ligands. Data are presented for copper(II) in association with 20 different ligands, including water, ammonia, pyridine, tetrahydrofuran, and benzene. For each $[Cu{\cdot}L_n]^{2+}$ 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. The data show considerable variation as a function of the composition and size of solvent molecule, with evidence of stable coordination shells containing between 2 and 8 molecules. In most instances, coordination shells containing more than four molecules can be attributed to the formation of an extended network of hydrogen bonds. Collisional activation of size-selected clusters reveals the presence of extensive ligand-to-metal electron transfer in the smaller complexes, and in several cases, charge transfer is also accompanied by chemical reactivity. The extent of charge transfer is frequently observed to be determined by the stability of the singly charged metal-containing product.

Introduction

Recent experiments on the association of singly charged metal ions with clusters of simple molecules have provided evidence of the formation of shell structure associated with the development of discrete solvation units.[1−5] Quantitative thermodynamic information is frequently restricted to the first solvation shell, which typically contains up to six molecules.[1,2] However, limitations in the techniques available for generating clusters have restricted most gas-phase studies of metal ion solvation to experiments on singly charged species.[1,2] In contrast, many metals of chemical and biochemical importance commonly occur in higher oxidation states, e.g., Cu(II), Ni(II), Fe(III) etc., but for these the study of individual solvent−ion complexes presents a number of experimental challenges. The main difficulty is that clustering techniques often rely on the condensation of solvent molecules around a central metal ion core. For Na^+ and Cs^+ this approach has been very successful;[3−5] however, for Cu^{2+}, charge transfer between the metal and solvent molecules takes place, and the result is solvated Cu^+ or some related, singly charged reaction product. Of the alternative techniques available for generating clusters containing multiply charged metal ions, Kebarle and co-workers[8−10] have demonstrated that electrospray can be used with considerable success to generate a range of solvated doubly and triply charged transition metal ions. Several groups have adopted this technique,[11−20] and in particular, Spence et al.[14] have successfully used electrospray as a means of studying the charge transfer spectra of multiply charged transition metal complexes. However, electrospray does appear to be restricted to ionic species already in solution prior to entry into a mass spectrometer, a limitation that could reduce the potential of the technique to undertake systematic studies of metal ion coordination and solvation. A partial solution to this problem has emerged from the work of Posey and co-workers,[14] whereby solvent molecules can be added to stable metal ion complexes generated via electrospray.

An alternative to electrospray is the pick-up technique,[21−25] where neutral metal−solvent complexes are prepared in a molecular beam, which is then ionized by high-energy electron impact. The success of this technique relies on the fact that multiply charged metal ions are generated after the metal has already been encapsulated within a stable solvent environment, which circumvents the need for any growth mechanism. Thus far, the pick-up method has been used to generate stable coordination complexes containing Mg(II),[21−23] Sr(II),[24] Cu(II),[25] Ag(II),[26] Au(II),[27] Mn(II),[28] Pb(II),[28] Cr(II),[28] and Ho(III)[29] in association with a very wide range of ligands. In several instances, for example, $[Mg{\cdot}(thf)_4]^{2+}$ and $[Ag{\cdot}(pyridine)_4]^{2+}$,[22,26] it has been observed that ions identified as the most stable metal−ligand configurations in the gas phase are analogous to the ionic cores of solid-state complexes.[30] These experiments have also provided an opportunity to explore the bonding of ligands that are not commonly used in transition metal chemistry, e.g., carbon dioxide and acetone.[26]

Presented here are the results of new experiments on Cu(II), where solvation of the ion has been studied in clusters composed of the ligands summarized in Table 1. For a ligand to stabilize Cu(II) successfully, the gain in solvation energy has to counteract the very large difference in energy between Cu(II) and Cu(I); otherwise reduction of the former will proceed very rapidly. Recent experiments on Cu(II) with electrospray have also been effective in generating stable complexes,[18−20] although several earlier attempts to produce $[Cu(H_2O)]^{2+}$ led to the observation of $CuOH(H_2O)_n{}^+$ ions.[10,16] In terms of behavior in bulk solvents, such as water or ammonia, Cu(II) is typically

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TABLE 1

ligand	α, Å$^{3\,a}$	μ, D^{b}	IE^{c}	$n_{\min}$	$I_{\max}$
water	1.45	1.85	12.61	3	8
methanol	3.29	1.70	10.85	3	8
ethanol	5.41	1.69	10.47	3	6
1-propanol	6.74	1.58	10.22	2	4
2-propanol	7.61	1.58	10.12	3	4
acetone	6.33	2.88	9.70	3	4
butanone	8.13	2.78	9.51	2	4
2-pentanone	9.93		9.38	2	4
2,4-pentadione	10.5		8.85	2	2
carbon dioxide	2.91		13.77	1	4
ammonia	2.81	1.47	10.16	2	8
pyridine	9.5	2.21	9.25	2	4
pyrazine	9.27		8.64	2	4
acetonitrile	4.40	3.92	12.19	2	4
thf		1.75	9.41	2	4
dioxane	8.60		9.91	3	3
benzene	10.0		9.24	2	2
benzonitrile	12.5	4.18	9.62	2	2
ethylenediamine	7.2	1.99	8.60		
nitric oxide	1.70	0.16	9.26		

[a] Polarizability. [b] Dipole moment. [c] Ionization energy.

expressed as having 6-fold coordination, i.e., $[\mathrm{Cu{\cdot}(H_2O)_6}]^{2+}$.[30] However, preliminary observations by this group on Cu(II) solvation in the gas phase showed that, for both water and ammonia, six is not the optimum coordination number[25,31] but that the most stable (intense) ions corresponded to $[\mathrm{Cu{\cdot}L_8}]^{2+}$ units. These results have been successfully interpreted by Bérces, Ziegler, and co-workers[32] using density functional theory, where they have been able to show that the basic solvation unit is a square planar $[\mathrm{Cu{\cdot}L_4}]^{2+}$ complex with four additional ligands hydrogen-bonded in the form of an extended second solvation shell. This picture provided stable structures for both $[\mathrm{Cu{\cdot}(H_2O)_8}]^{2+}$ and $[\mathrm{Cu{\cdot}(NH_3)_8}]^{2+}$, with neither complex exhibiting any tendency for ligands to bind to equatorial positions on the metal ion.[32] As a result of these observations, it was considered appropriate to extend the experiments to other hydrogen-bonded solvents. New results are presented for a range of alcohols coordinated to Cu(II), where their behavior can be attributed to a combination of hydrogen-bonding and steric interactions. In contrast, results on the solvation of Cu(II) in aprotic solvents, such as acetone and acetonitrile, are dominated by the presence of stable $[\mathrm{Cu{\cdot}L_4}]^{2+}$ structures, with the absence of strong intermolecular forces restricting the appearance of larger solvation units.

Results are also presented of experiments on the fragmentation patterns of $[\mathrm{Cu{\cdot}L}_n]^{2+}$ complexes. In most instances, the collisional activation of a small ion (≤ 6) leads to extensive charge transfer, and as the ions increase in size, this behavior is replaced by the unimolecular loss of neutral ligands. For several complexes, charge transfer is accompanied by a chemical reaction that frequently involves decomposition of the (charged!) ligands.

Experimental Section

The experiments detailed here utilize a commercial Knudsen effusion cell in conjunction with a cluster beam apparatus and a VG ZAB-E double-focusing, reverse-geometry mass spectrometer. An extensive description of the instrumentation used for generation, resolution, and detection of the cluster beam has been provided in previous work.[26,33] Of particular relevance to this work is the use of a pick-up technique by which mixed neutral clusters consisting of copper and ligand molecules (L) are produced. This initial step enables $[\mathrm{Cu{\cdot}L}_n]^{2+}$ complexes to be produced within the ion source of the mass spectrometer. A mixture of argon as a carrier gas and a solvent undergoes supersonic expansion through a pulsed conical nozzle. For ammonia, carbon dioxide, and ethene, high-pressure cylinders containing 99% Ar and 1% solvent were used to produce the required 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 arrangement enabled solvent vapor to become entrained in the argon stream, providing the appropriate gas mixture for the expansion process. For solvents with relatively high vapor pressures, the reservoir was cooled in ice. A carrier gas backing pressure of approximately 45 psi was used in most experiments, and previous work has shown the use of argon in this role to be crucial to success of the pick-up technique.[21−27,34]

The resultant cluster beam was collimated by use of a 1 mm diameter skimmer before passing through a region containing copper vapor produced from a Knudsen effusion cell operating at 1400 °C. This and previous work suggests 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 copper 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 ions that do not arise from material originating from within 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 mass/charge ratio, within the magnetic sector of the instrument. Doubly charged species are transmitted through the magnetic sector at fields that 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 have been 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.[35] 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. 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 with a Daly

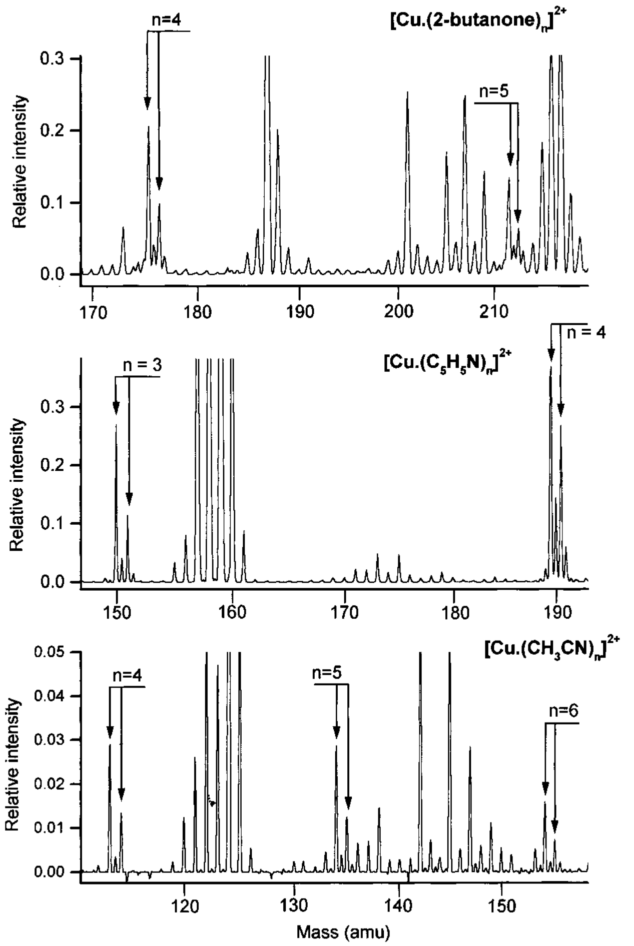

Figure 1. Selection of mass spectra recorded with the pickup technique to prepare Cu(II) complexes. In each case the peaks identified correspond to ^{63}Cu and ^{65}Cu. (a, top) [Cu•(2-butanone)$_{4,5}$]$^{2+}$; (b, middle) [Cu•(pyridine)$_{3,4}$]$^{2+}$; (c, bottom) [Cu•(CH$_3$CN)$_{4-6}$]$^{2+}$.

scintillation detector, where photon counting methods can be used to detect very 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 intensities are of 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 copper 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. Separate measurements on ^{63}Cu and ^{65}Cu have also been used to confirm the intensity profiles presented below.

Figure 1 shows short sections of mass spectra recorded for a series of [Cu•L$_n$]$^{2+}$ systems. In addition to the ions of interest, there are also present substantial signals from those ions considered to be byproducts of the technique being used to prepare the complexes. In most instances, these byproducts can be identified as L$_n^+$, L$_n$H$^+$, and L$_n^{+}$•Ar$_m$ clusters; however, some L$_n^+$ clusters also have a significant range of decomposition products. The successful observation of [Cu•L$_n$]$^{2+}$ complexes relies on several factors, including the absence of any significant overlap with the ions identified above and, where possible, the presence of peaks at half-integer mass positions. In the case of nitrogen-containing ligands, the latter only occur when n is an even number.

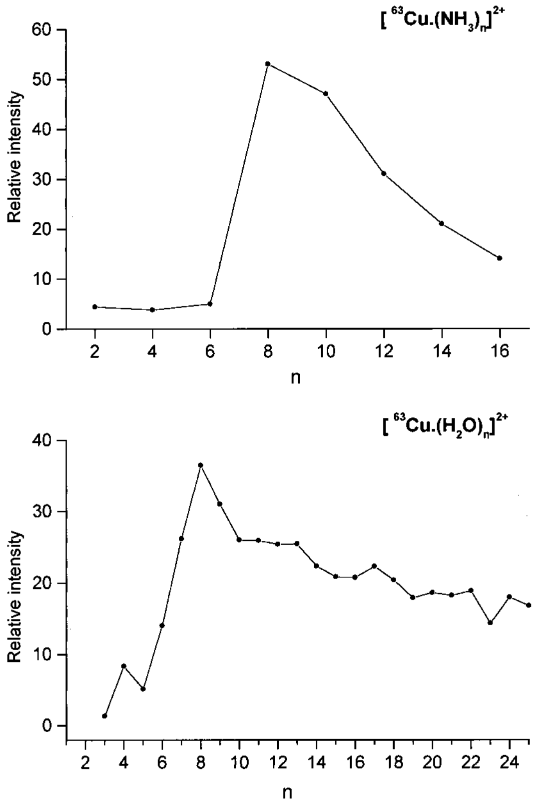

Figure 2. Intensity profiles recorded for (a, top) [Cu•(NH$_3$)$_n$]$^{2+}$ and (b, bottom) [Cu•(H$_2$O)$_n$]$^{2+}$ plotted as a function of n.

Results and Discussion

Experiments have been undertaken on the solvation of Cu(II) in association with the 20 ligands listed in Table 1. Also listed are several physical properties of the ligands that could have an influence on the stability of a given complex. In two instances it was not possible for a ligand to stabilize Cu(II), and the significance of these examples will be discussed later. Figure 2 summarizes intensity data recorded previously for [Cu•(H$_2$O)$_n$]$^{2+}$ and [Cu•(NH$_3$)$_n$]$^{2+}$ complexes, showing [Cu•L$_8$]$^{2+}$ to be the most intense (stable) ion, a result that has been interpreted by Bérces et al.[32] As a function of size (n), the ion intensity profile of a typical [M•L$_n$]$^{2+}$ system follows a very characteristic pattern, which is influenced by a number of common factors. First, complexes containing just one or two ligands are frequently either absent or have very low intensities because they are unstable with respect to charge transfer. The ionization energy of Cu$^+$ is 20.29 eV, compared with that of most ligands at ~9–12 eV (see Table 1), and a critical number of ligands is required to accommodate this difference. It is only with the development of a solvent shell that many multiply charged metal–ligand complexes achieve optimum stability. Particularly stable metal–ligand combinations are associated with high ion intensities (magic numbers), and it has recently been shown that large [M•L$_n$]$^{2+}$ complexes will preferentially fragment down to a stable structure following electronic excitation.[36] Finally, the decline in intensity seen for larger ions is a characteristic feature of cluster experiments in general. For each [M•L$_n$]$^{2+}$ system it has been possible to identify two important quantities: a minimum stable size, $n_{\min}$, and the most stable combination, $I_{\max}$, and

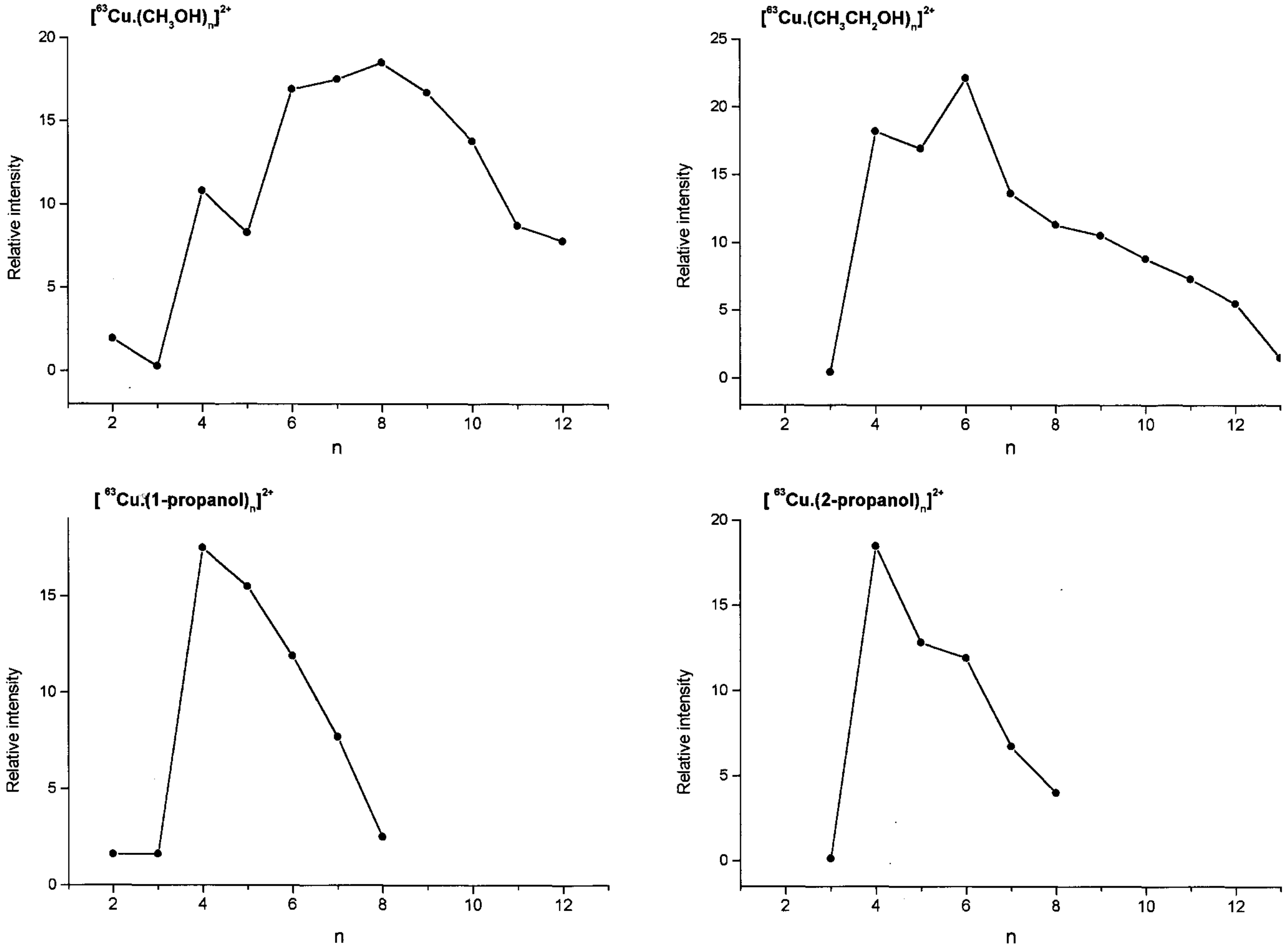

Figure 3. Intensity profiles recorded for (a, upper left) $[Cu\cdot(CH_3OH)_n]^{2+}$, (b, upper right) $[Cu\cdot(CH_3CH_2OH)_n]^{2+}$, (c, lower left) $[Cu\cdot(1\text{-propanol})_n]^{2+}$, and (d, lower right) $[Cu\cdot(2\text{-propanol})_n]^{2+}$, each plotted as a function of n.

theses values are summarized in Table 1 for the Cu(II) complexes discussed here.

Cu(II) with Hydrogen-Bonded ROH Solvents. Since very marked differences were observed between the coordination of Cu(II) in bulk solutions of ammonia and water and intensity profiles recorded in the gas phase, new experiments have been undertaken on the association of Cu(II) with other hydrogen-bonded ligands. Figure 3 presents data recorded for complexes with the alcohols: methanol, ethanol, 1-propanol, and 2-propanol, where the results exhibit a clear trend in I_{max}. Cu(II) appears capable of accommodating eight methanol ligands in a manner similar to that observed for water and ammonia. Such an arrangement would be consistent with the results of Bérces et al.,[32] where four methanol molecules would form a primary square-planar coordination shell, which would then retain a further four molecules via hydrogen bonds. However, as calculations have shown, the strengths of the latter are greatly enhanced by the presence of the double charge on the central metal ion.[37] In addition, Bérces et al.[32] attributed the stability of this outer shell to the formation of double acceptor bonds by the outer shell of molecules, and similar hydrogen-bonded configurations have been identified in $Na^+(CH_3OH)_n$ clusters.[4-7] Given that both $[Cu\cdot(CH_3OH)_4]^{2+}$ and $[Cu\cdot(CH_3OH)_6]^{2+}$ are comparatively intense, it is suggested that the relative stability of $[Cu\cdot(CH_3OH)_8]^{2+}$ is not as high as that of the equivalent water or ammonia structures.

With the formation of $[Cu\cdot(CH_3CH_2OH)_n]^{2+}$ complexes, it can be seen that there is a downward shift in maximum intensity to $I_{max} = 6$, with $[Cu\cdot(CH_3CH_2OH)_4]^{2+}$ also becoming more prominent. Finally, for 1- and 2-propanol both Cu(II) complexes exhibit intensity maxima at $n = 4$, a result that is consistent with those ligands which do not form hydrogen bonds (see below). This downward trend in I_{max} is attributed to steric factors, with the increased complexity of each ligand making it more difficult to form a stable outer shell of hydrogen-bonded molecules. In all of these systems, it is the oxygen atom on each molecule that is coordinated to the central copper ion; at the same time, however, the hydroxyl H atom is required to participate in the formation of hydrogen bonds with subsequent solvation shells, a process that must become increasingly more difficult as the length of the hydrocarbon chain increases.

To complement the intensity data, an extensive range of MIKE scans have been performed on size-selected $[Cu\cdot L_n]^{2+}$ complexes following collisional activation. The observed fragment ions take one of two forms, either (a) doubly charged ions resulting from unimolecular fragmentation of the parent ion by the loss of neutral ligand molecules or (b) singly charged ions produced by charge transfer followed by Coulomb explosion. The latter ions are detected at double the laboratory frame kinetic energy of a mass coincident with the daughter ion resulting from process a. A further characteristic of the Coulomb explosion processes is that, following charge transfer, repulsion between the two singly charged species is accompanied by a large release of kinetic energy, which leads to a broadening in the peak profiles. Unfortunately, this broadening also leads to a loss of

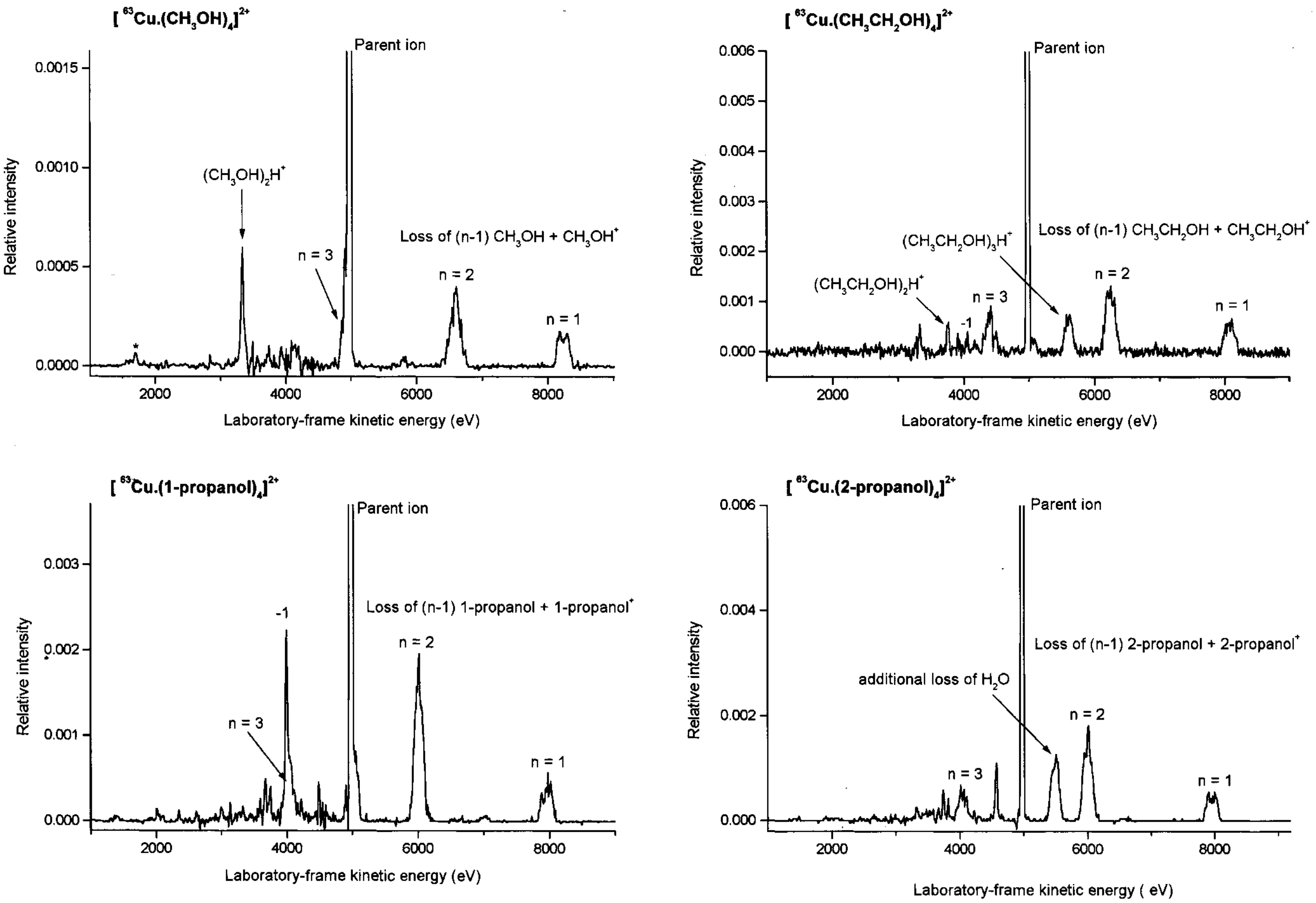

Figure 4. Mass-analyzed ion kinetic energy (MIKE) spectra recorded as a function of laboratory-frame kinetic energy for (a, upper left) [^{63}Cu$\cdot$(CH$_3$OH)$_4$]$^{2+}$, (b, upper right) [^{63}Cu$\cdot$(CH$_3$CH$_2$OH)$_4$]$^{2+}$, (c, lower left) [^{63}Cu$\cdot$(1-propanol)$_4$]$^{2+}$, and (d, lower right) [^{63}Cu$\cdot$(2-propanol)$_4$]$^{2+}$. The peaks identified by −1 correspond to the loss of a single neutral ligand.

resolution, which prevents the accurate assignment of reaction products involving the addition or loss of a proton (see below).

As distinct from unimolecular loss, collisional activation also provides three identifiable routes leading to the appearance of reaction products: (i) Chemical processes induced by the presence of the doubly charged metal core and not involving charge transfer. Previous experiments have shown that the products of such reactions are inclined to be stable ligands.[21,23] (ii) Reactions accompanied by charge transfer and usually associated with the displacement of a counterion in the form of e^- or H^- in the case of alkanes[38,39] and HO^- or RO^- in the case of water or an alcohol.[15,21,23] A slightly different viewpoint would be to consider the metal ion acting as a strong Lewis acid, and polarization of the electron cloud on, for example, the oxygen atom of H_2O leads to the loss of a proton into either the gas phase or the surround shell of solvent molecules.[40] Since the loss of just H^+ is not observed very frequently, it is quite possible that the latter process is enhanced if the proton is already engaged in hydrogen bonding and is lost as $(ROH)_mH^+$ for $m \geq 1$ (see below). (iii) Reactions resulting from the presence of a singly charged metal ion following charge transfer. Where applicable these processes might be very similar to those seen in earlier studies of metal ion−molecule reactive collisions.[41] Given the large energy differences often seen between the various ionization levels involved in charge transfer (see Table 1), there is the possibility of excited states of the singly charged metal ion being accessed. However, should this be the case, then the lifetimes of these electronic states with respect to radiative and/or nonradiative decay would have to be greater than the time scale necessary for any chemical reactions in which they are to participate.

Figure 4 shows the results of MIKE scans of $[Cu\cdot L_4]^{2+}$ complexes for L = methanol, ethanol, 1-propanol, and 2-propanol, with proposed assignments for the majority of the observed fragments. The parent ion intensity data suggest that $[Cu\cdot L_4]^{2+}$ structures are of either primary or secondary stability depending on the solvent. In support of this, neutral loss of solvent molecules from all of the complexes is extremely weak when compared with the magnitudes of the charge-transfer products. The latter process in $[Cu\cdot L_4]^{2+}$ complexes appears to be accompanied by the loss of one, two, and three ligands for all four solvents. As an indication of the subtle nature of the interaction between Cu(II) and the ligands in terms of stabilizing the double charge, it can be seen that in all cases the $[Cu\cdot L_4]^{2+}$ complexes undergo charge transfer with the loss of just a single molecule. While unimolecular decay is an expected outcome following internal excitation, the route to charge transfer is less obvious. Two possible mechanisms exist: (i) A complex may undergo unimolecular decay until it reaches n_{min}, at which point it becomes unstable and ligand-to-metal charge- (electron-) transfer (LMCT) occurs. However, since charge transfer is seen following the loss of just one ligand from complexes as large as $[Cu\cdot L_6]^{2+}$, the fragmentation data would not appear to support such a proposal. It is, however, quite possible that a mechanism such as this may operate in the small ($n \leq 4$) complexes. The probability of observing charge transfer does decline very rapidly beyond $[Cu\cdot L_6]^{2+}$ complexes. (ii) An alternative is that collisional activation promotes internal electronic excitation within a ligand, and this in turn facilitates LMCT. Given that center-of-mass collision energies (with air as the collision gas) are of the order of ~1000 eV, electronic excitation is certainly possible; however, for large ($\sim Ar_{25}^+$) argon cluster ions it has been shown that under conditions comparable to those used here, vibrational excitation is favored over electronic.[42,43] A significant difference between the rare gases and those molecules being considered here is that electronic excited states in the latter occur at very much lower energies than those found in argon. Evidence in support of such a mechanism has been found recently in a laser-induced photofragmentation study of small $[Ag\cdot(pyridine)_n]^{2+}$ complexes.[36] Following the electronic excitation ($\pi \rightarrow \pi^*$) of a pyridine molecule in the first solvation shell at UV wavelengths, LMCT was observed to be the dominant decay mechanism. Therefore, by analogy with the laser experiments, collisional activation could promote LMCT if the collision partner has access to molecules in the first solvation shell, which then undergo electronic excitation. The constraint imposed by access to the first solvation shell would also help to explain the size effect identified above.

Unfortunately, the widths of the charge-transfer peaks are sufficient as to leave some uncertainty regarding assignment of fragments in Figure 3. Thus, the peak labeled $n = 2$ for methanol could correspond to any of the following metallic fragments: (a) $CuOCH_3^+\cdot CH_3OH$, (b) $CuH^+\cdot(CH_3OH)_2$, or (c) $Cu^+\cdot(CH_3OH)_2$, all of which lie within ±1 amu of c, the straightforward charge-transfer product. When expanded, comparable data for Mg(II) and Sr(II) have revealed the presence of composite peaks,[23,24] which in small complexes can be resolved into identifiable components.[44] On the basis of evidence from the study by Kohler and Leary[15] on the collision-induced reactions of Co(II) and Mn(II) complexes with methanol, the formation of $CuOCH_3^+\cdot CH_3OH$ would appear the most obvious product. Such a reaction would yield $(CH_3OH)_2H^+$ as the complementary ion, which is known to be very stable and can in fact be clearly identified in the MIKE spectrum (Figure 4a). It would also be possible to rationalize the presence of $CuOCH_3^+\cdot CH_3OH$ in terms of Cu(II) acting as a Lewis acid [in this respect, Cu(II) and Co(II) might be viewed as acids of comparable strength].[45] However, an important consideration when comparing Cu^+ with either Co^+ or Mn^+ as charge-transfer products is that the ground-state electron configuration of Cu^+ ($3d^{10}$) does not easily lend itself to formation of either $CuOCH_3^+$ or CuH^+. Such ions would require electron promotion to the ^3D state ($3d^94s^1$), which in the atomic ion lies 2.7 eV above the ground state.[46] In this respect, it is interesting to note that $CuOH^+$ is frequently observed following attempts to generate Cu(II)/water complexes via electrospray.[10,16] A similar pattern of behavior to methanol is seen in the MIKE scan of $[Cu\cdot(ethanol)_4]^{2+}$ (Figure 4b), but this time the counterion is $(CH_3CH_2OH)_3H^+$.

One final aspect of the charge-transfer results in Figure 4 that is of significant interest is the presence of a feature in the 2-propanol spectrum that appears to correspond to the loss of $[L_2\cdot H_2O]^+$. The implication is that charge transfer is accompanied by a chemical reaction that leads to the dehydration of an alcohol molecule, i.e.

$$[Cu(2\text{-}PrOH)_4]^{2+} \rightarrow Cu^+\cdot C_3H_6\cdot 2\text{-}PrOH + 2\text{-}PrOH + 2\text{-}PrOH^+ + H_2O \quad (1)$$

As with the other reactions discussed above, there is some uncertainty as to the exact nature of the reaction products. However, it would appear from previous data that, in instances where reaction products are required to form covalent bonds with Cu^+, the bond dissociation energies are low and therefore may not have an important influence on determining the outcome of a reaction. Two previous studies of the reactions of Cu^+ with alcohols have shown evidence of a mixture of dehydration and dehydrogenation processes.[47,48] A study by Weil and Wilkins[48] gave H_2 as the main product from the reaction $Cu^+ + EtOH$, whereas 1-PrOH and 2-PrOH with Cu^+ gave H_2, H_2O, and C_3H_6 as neutral products. None of the reactions led to the appearance of CuH^+, CuR^+, $CuOR^+$, or $CuOH^+$ as product ions

Studies of the reactions of singly charged metal ions with alcohol molecules have identified several possible pathways leading to dehydration.[49−55] In the first, a single molecule undergoes metal ion insertion into a C−O bond, which is followed by β-hydrogen atom transfer.[49,50] A second possibility is for two alcohol molecules to undergo a condensation reaction, which would leave Cu^+ ligated to a single ether molecule (pathway not shown, but the empirical formula of the ion would be identical to that given in eq 1). The work of Castleman and co-workers[51,52] and Draves and Lisy[53] have shown that metal ion/methanol complexes can exhibit a dehydration reaction, but initiation of the process requires the presence of at least eight molecules. Finally, for closed-shell ions, such as Cu^+ ($3d^{10}$), it has been proposed that reactivity proceeds via an ion−dipole mechanism.[54,55] It is interesting to note that, in comparison to the 2-propanol data, there is no evidence of a dehydration reaction in $[Cu(1\text{-}PrOH)_4]^{2+}$ cluster ions. However, a number of metal ions have demonstrated a greater propensity to dehydrate 2-propanol rather than 1-propanol; a result that has been attributed to the weaker C−OH bond in the former, which facilitates the initial OH abstraction necessary for the ion/dipole mechanism to proceed.[55]

Figure 5 shows data recorded following the collisional activation of $[M\cdot L_6]^{2+}$ complexes consisting of each of the alcohols discussed above. With the increased number of ligands, the loss of neutral molecules is observed to be in competition with charge transfer. The fragmentation patterns are dominated by the loss of one and two neutral molecules, which would support the picture derived from parent ion intensity measurements, in that $[Cu\cdot L_4]^{2+}$ ions represent an underlying stable unit. As identified above for the $[Cu\cdot L_4]^{2+}$ ions, $[Cu\cdot(CH_3OH)_6]^{2+}$ shows evidence of $(CH_3OH)_2H^+$ as a charge-transfer product, $[Cu\cdot(ethanol)_6]^{2+}$ has $(CH_3CH_2OH)_3H^+$ as a product, and $[Cu\cdot(2\text{-}propanol)_6]^{2+}$ exhibits the dehydration reaction seen earlier. In all cases, the charge-transfer products have lower intensities than those seen for $[Cu\cdot L_4]^{2+}$ complexes. It is also interesting to note that charge-transfer processes leading to the loss of just ROH_2^+ have disappeared completely but that the relative intensities of signals arising from more extensive fragmentation have increased.

Data recorded following the collisional activation of alcohol-containing complexes larger than those discussed above are dominated by the loss of neutral ligands. In many instances the ions fragment down to the $[Cu\cdot L_4]^{2+}$ unit, which once again confirms the underlying stability of this particular configuration. All the large ions show some evidence of charge-transfer reactions; however, these channels are significantly reduced in intensity when compared with the examples seen from the $[Cu\cdot L_4]^+$ and $[Cu\cdot L_6]^+$ complexes. In addition, the promotion of charge transfer frequently requires the removal of three or more ligands. Such behavior could be predicted from a consideration of the increased stability of the ion, where the additional

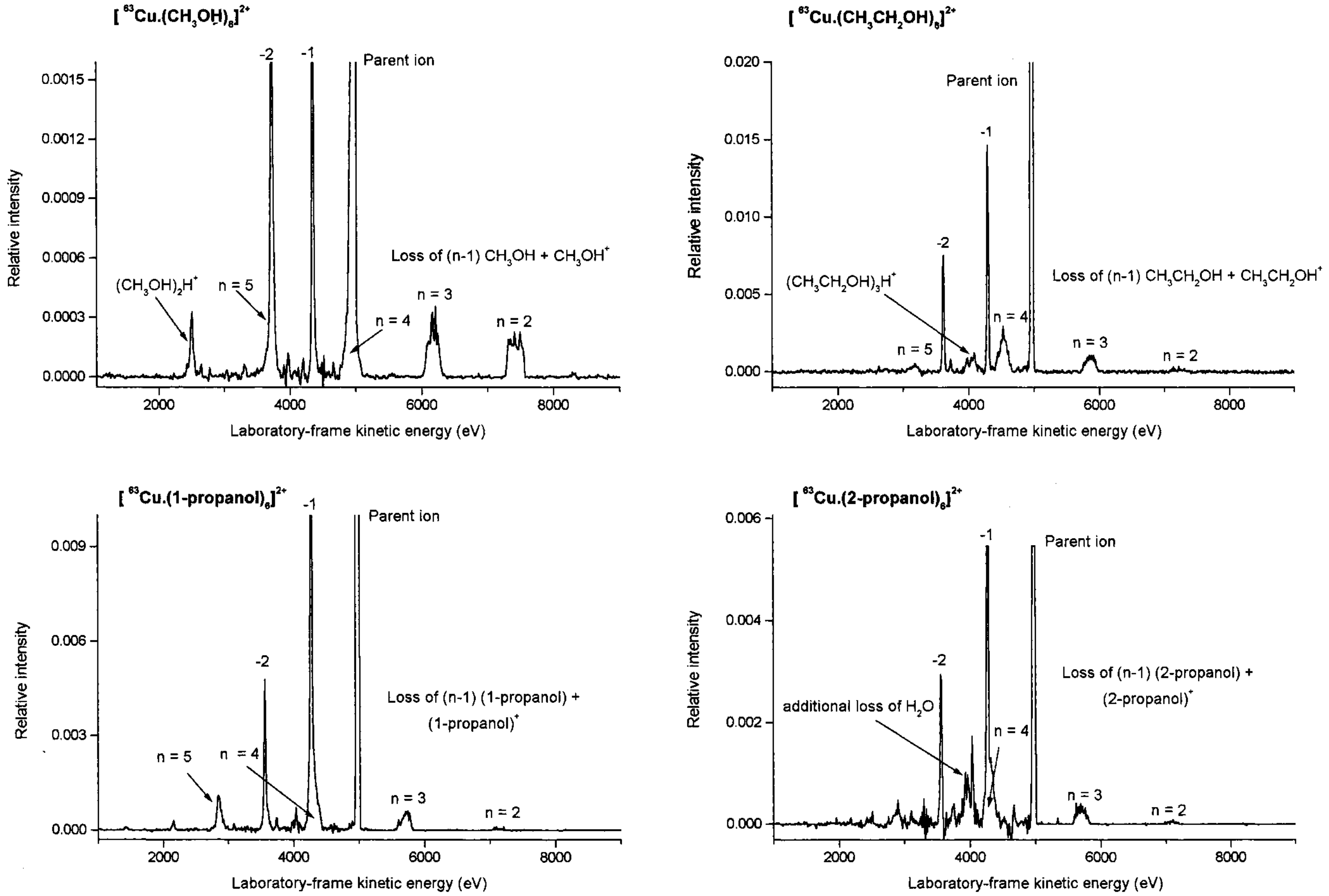

Figure 5. Mass-analyzed ion kinetic energy (MIKE) spectra recorded as a function of laboratory-frame kinetic energy for (a, upper left) $[^{63}Cu{\cdot}(CH_3OH)_6]^{2+}$, (b, upper right) $[^{63}Cu{\cdot}(CH_3CH_2OH)_6]^{2+}$, (c, lower left) $[^{63}Cu{\cdot}(1\text{-propanol})_6]^{2+}$, and (d, lower right) $[^{63}Cu{\cdot}(2\text{-propanol})_6]^{2+}$. The peaks identified by -1 and -2 correspond to the loss of one and two neutral ligands, respectively.

solvation energy presents a barrier that has to be surmounted by collisional activation if charge transfer is to be promoted.[26]

Cu(II) in Aprotic Solvents. Figure 6 shows intensity distributions recorded following the solvation of Cu(II) with the solvents acetone, pyridine, tetrahydrofuran, and acetonitrile. In each case, the distribution is dominated by a comparatively intense $[Cu{\cdot}L_4]^{2+}$ unit, and there is a very rapid decline in intensity as the complexes increase in size. There is no evidence of the extended secondary solvation network seen for the hydrogen-bonded ligands. In keeping with the analogous solid-state compounds,[30] we would propose that the $[Cu{\cdot}L_4]^{2+}$ units are square planar but that, in the case of pyridine, for example, the rings may not necessarily all lie in the same plane.

Figure 7 shows a selection of MIKE spectra recorded for three $[Cu{\cdot}L_4]^{2+}$ complexes containing either acetone, 2-butanone, or 2-pentanone. When these are compared with the corresponding data given above for the alcohols, each scan shows two quite distinct differences: first, in all cases there is a significant unimolecular contribution, and second, the charge-transfer reaction is dominated totally by the loss of two ligands to form $Cu^+{\cdot}L_2$, to the extent that the charge-transfer product $Cu^+{\cdot}L_3$ is virtually nonexistent. Since $Cu^+{\cdot}L_2$ complexes are known to be very stable in the condensed phase,[30] this factor is clearly having a very strong influence on the gas-phase reaction pathway. Only $[Cu{\cdot}(1\text{-propanol})_4]^{2+}$ (Figure 4c) shows some evidence of a similar pattern of behavior.

Figure 8 shows an intensity profile recorded for $[Cu{\cdot}(CO_2)_n]^{2+}$ complexes plotted as a function of n, where the pattern of coordination is very similar to that seen for (more traditional!) aprotic ligands. Our experiments have shown carbon dioxide to be an unexpectedly good ligand,[25,28] a capability that has been attributed to the molecule having a comparatively high ionization energy.[25] In the case of Cu(II), just one molecule is sufficient to stabilize the ion. Similar stable complexes have been seen with Ag(II) and Au(II),[25,28] which led to the speculation that supercritical CO_2 might be a suitable medium for containing these and other ions in high oxidation states. Figure 9 shows a MIKE spectrum recorded following the collisional activation of $[Cu{\cdot}(CO_2)_4]^{2+}$. Compared with previous scans of this type, Figure 9 shows several interesting features: first, the charge transfer peaks are relatively narrow, which could be due to a combination of reduced difference in ionization energy and the possibility that some fraction of the Coulomb repulsion energy is taken up as vibrational excitation in the departing CO_2 molecule(s) and ion. Internal excitation on a repulsive surface is known to occur in dynamical processes in neutral systems.[56] Second, there is evidence of a chemical reaction, where at least two peaks in the MIKE spectrum can be assigned to the process

$$[Cu{\cdot}(CO_2)_4]^{2+} \rightarrow CuO^+{\cdot}(CO_2)_n + CO_2^{\ +} + (2-n)CO_2 + CO$$

with $n = 1$ and 0. Finally, there is a peak that has been assigned to the charge-transfer step:

$$[Cu{\cdot}(CO_2)_4]^{2+} \rightarrow Cu^+{\cdot}(CO_2)_2 + (CO_2)_2^{\ +}$$

A similar cluster–metal electron-transfer process has been

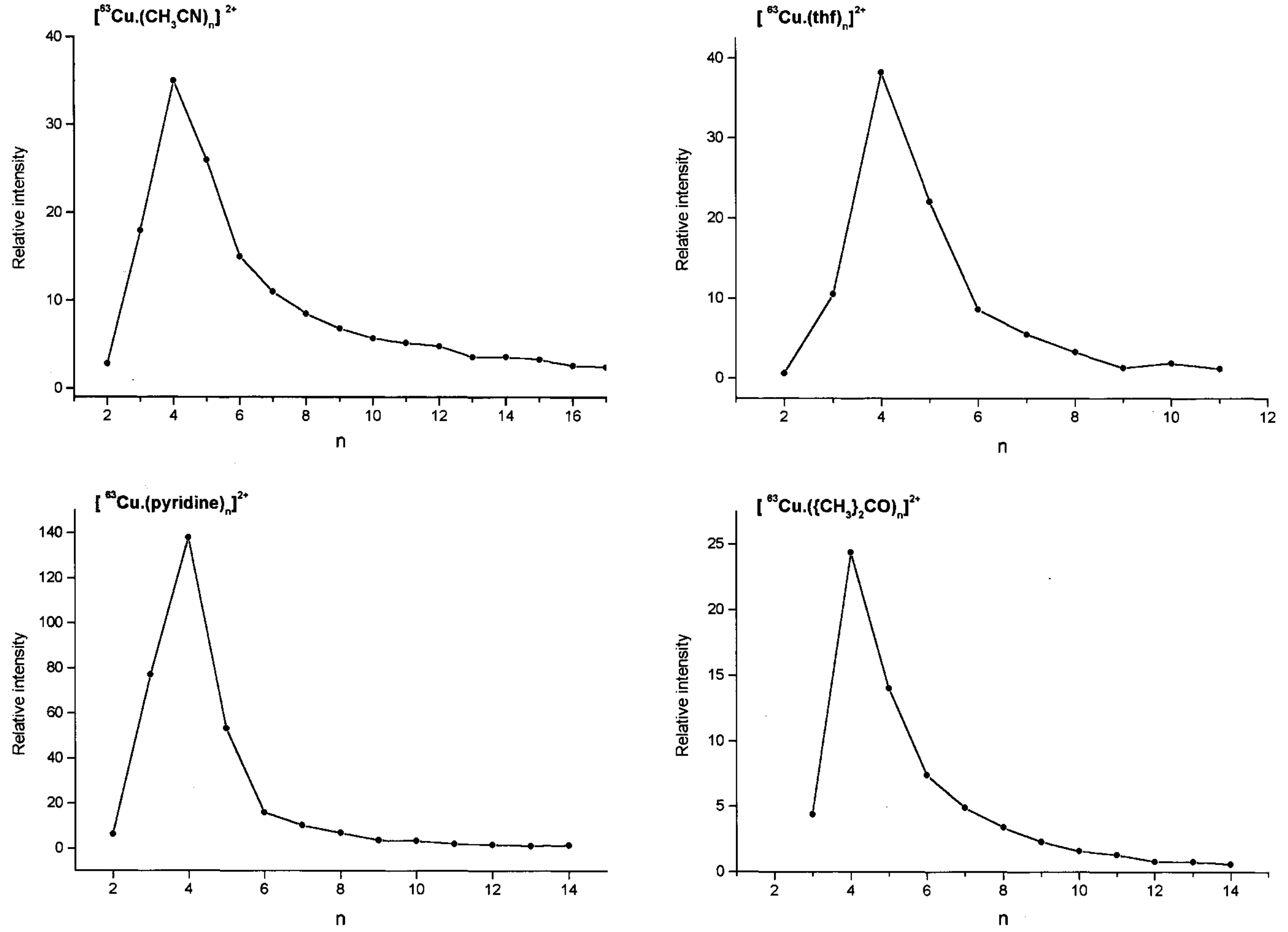

Figure 6. Intensity profiles recorded for (a, upper left) $[Cu{\bullet}(CH_3CN)_n]^{2+}$, (b, upper right) $[Cu{\bullet}(thf)_n]^{2+}$, (c, lower left) $[Cu{\bullet}(pyridine)_n]^{2+}$, and (d, lower right) $[Cu{\bullet}(\{CH_3\}_2CO)_n]^{2+}$, each plotted as a function of n.

identified in $[Mn{\bullet}(pyridine)_4]^{2+}$ clusters[57] and has been attributed to the comparatively small difference in ionization energies between the metal and the ligand molecule. Although some of the alcohol ligands discussed above displayed $(ROH)_nH^+$ charge-transfer fragments, the mechanism responsible for their formation is considered to be slightly different form that of, for example, $(CO_2)_2{}^+$. In the former the molecules are considered to be already associated via a hydrogen-bonded network prior to charge transfer, whereas for aprotic ligands, electron transfer is accompanied by association with nearest-neighbor molecules, and the process appears to be restricted to the formation of cluster ions containing ≤3 molecules.[57]

Finally, Figure 10 shows two examples of MIKE spectra recorded following the collisional activation of (a) $[Cu{\bullet}(C_2H_4)_3]^{2+}$ and (b) $[Cu{\bullet}(C_6H_6)_2]^{2+}$. In both cases, these are the most intense copper/ligand combinations observed in the mass spectra. In the case of benzene, $[Cu{\bullet}(C_6H_6)_2]^{2+}$ is the only ion observed. which suggests that the structure may consist of a sandwichlike arrangement with benzene rings positioned above and below a central metal ion. This arrangement of molecules would be similar to that seen in condensed phase transition metal−benzene complexes, e.g., $(C_6H_6)_2Cr^+$;[58] however, in the case of Cu(II)/benzene complexes in the solid state, these appear to have been formed under conditions where they cannot be fully characterized.[59,60] Similar sandwich structures have also been identified for singly charged transition metal−benzene clusters in the gas phase.[61,62] As the MIKE scan shows, there is little or no evidence for the loss of a single neutral molecule. What is interesting, however, is that the shape of the charge-transfer peak is identical to that recorded for $[Ag{\bullet}(C_6H_6)_2]^{2+}$,[26] which suggests the presence of two or three different chemical charge-transfer pathways separated in mass by either H_2 or $2H_2$.

Previous examples of metal−ethene complexes involving π-bonded systems have been interpreted in terms of a filled metal orbital overlapping with a vacant molecular π^* orbital, accompanied by electron flow back to the metal via a vacant atomic orbital overlapping with a molecular π orbital.[30] For a bare metal atom, such as Cu(II), the optimum number of π-bonded ligands would be three, and these would utilize one of either the $3d_{xy}$, $3d_{xz}$, or $3d_{yz}$ orbitals for each π^* overlap and one of either the $4p_x$, $4p_y$, or $4p_z$ orbitals for each π overlap. As shown earlier, $[Cu{\bullet}(C_2H_4)_3]^{2+}$ is the most stable combination, and thereafter,[31] the relative intensities of larger complexes decline rapidly. The intensity profile also shows the signal for $[Cu{\bullet}(C_2H_4)_2]^{2+}$ to be comparable in strength to that observed for the trimer,[31] which might account for the comparative ease with which the latter loses C_2H_4 (Figure 10b). By comparison, the charge-transfer peaks shown in Figure 10b are very weak, a situation that contrasts with some of the other results presented following MIKE scans on small $[Cu{\bullet}L_n]^{2+}$ complexes. The picture of bonding outlined above could accommodate participation by smaller complexes; indeed, existing solid-state data cover organometallic compounds containing between one and three ethene molecules.[30]

In addition to the ligands discussed above, there are three further examples that warrant attention. Both ethylenediamine

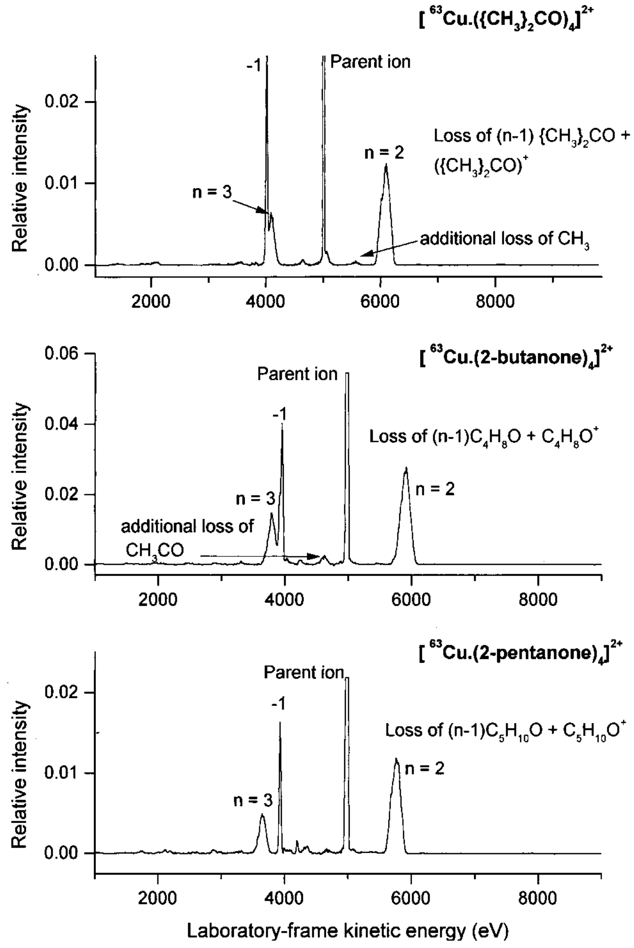

Figure 7. Mass-analyzed ion kinetic energy (MIKE) spectra recorded as a function of laboratory-frame kinetic energy for (a, top) $[^{63}\text{Cu}\cdot(\{\text{CH}_3\}_2\text{CO})_4]^{2+}$, (b, middle) $[^{63}\text{Cu}\cdot(\text{2-butanone})_4]^{2+}$, and (c, bottom) $[^{63}\text{Cu}\cdot(\text{2-pentanone})_4]^{2+}$. The peaks identified by -1 correspond to the loss of a single neutral ligand.

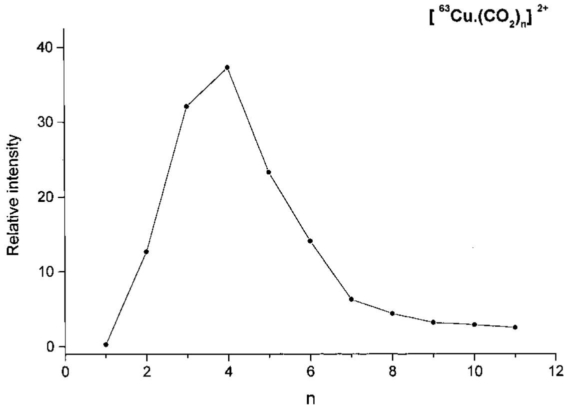

Figure 8. Intensity profile recorded for $[\text{Cu}\cdot(\text{CO}_2)_n]^{2+}$ ions, plotted as a function of *n*.

and 2,4-pentadione traditionally act as bidentate ligands in the condensed phase;[30] however, only one of these has proved successful at forming a stable doubly charged complex in the gas phase. Failure to observe a stable unit with ethylenediamine is not too surprising; the molecule has a low IE, which means that each attachment would have to stabilize the complex to a very high degree. Since up to two ligands might be expected to attach themselves, each would have to contribute to the complex a stabilization energy of 3.5 eV. In the case of 2,4-pentadione, we are clearly unable to tell from the data available whether

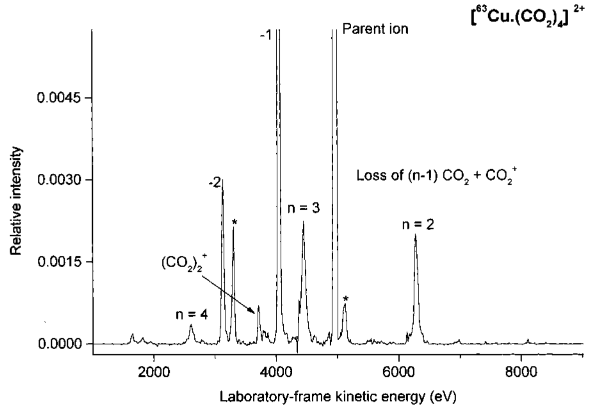

Figure 9. Mass-analyzed ion kinetic energy (MIKE) spectra recorded as a function of laboratory-frame kinetic energy for $[^{63}\text{Cu}\cdot(\text{CO}_2)_4]^{2+}$. The peaks identified by -1 and -2 correspond to the loss of one and two neutral ligands, respectively. The peaks identified by asterisks correspond to charge transfer accompanied by the additional loss of CO.

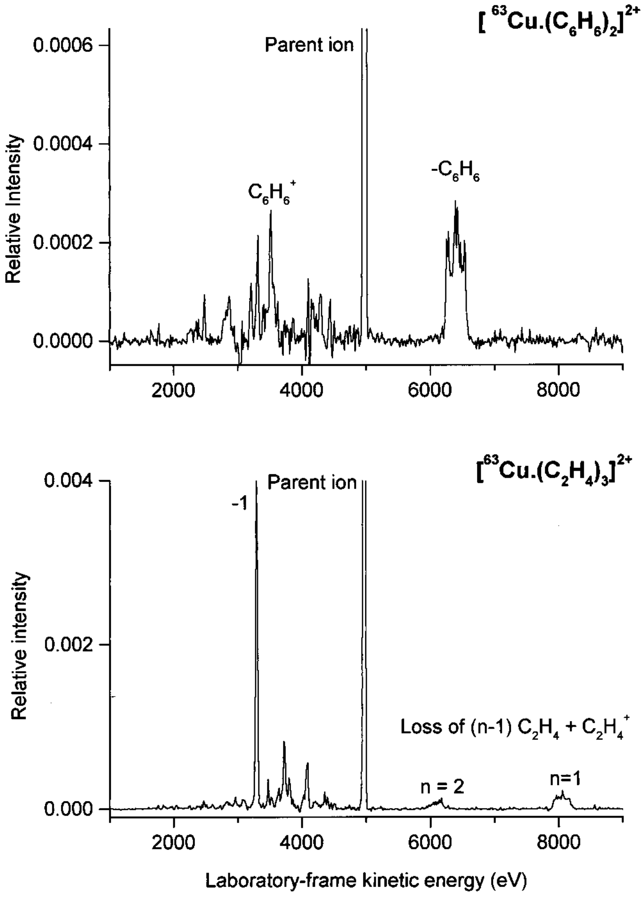

Figure 10. Mass-analyzed ion kinetic energy (MIKE) spectra recorded as a function of laboratory-frame kinetic energy for (a, top) $[^{63}\text{Cu}\cdot(\text{C}_6\text{H}_6)_2]^{2+}$ and (b, bottom) $[^{63}\text{Cu}\cdot(\text{C}_2\text{H}_4)_3]^{2+}$. The peak identified by -1 corresponds to the loss of a single neutral ligand.

both points of contact within each molecule are indeed attached to Cu^{2+}. However, on the asis of the data presented for unidentate ligands in Table 1, it can be seen that those with ionization energies and polarizabilities comparable to 2,4-pentadione all require attachment to at least two sites to stabilize the ion. This observation, together with the fact that the ion with maximum intensity contains two 2,4-pentadione molecules, does suggest bidentate behavior. This being the case, then the complex would match the 4-fold coordination seen with 10 of the other (unidentate) ligands. Very similar behavior was seen in the case of Mg^{2+},[63] where ethylenediamine also failed to form a stable complex but 2,4-pentadione exhibited an identical pattern of coordination to that seen here. There is a counterargument to be made against bidentate behavior, which is that if one end of a ligand becomes attached, then in the gas phase the probability of a second attachment is probably going to be quite low, the reasons being 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 MIKE scan of $[Cu{\cdot}(2,4\text{-pentadione})_2]^{2+}$ showed no evidence of losing a single neutral molecule, which could be taken as a sign of stability, but did exhibit a charge-transfer peak corresponding to the loss of a single charged molecule.

The final ligand to be discussed is nitric oxide. Although stable transition metal complexes containing NO do exist,[30] it was not possible to stabilize Cu(II) with one or more of the molecules in the gas phase. A reason for this behavior can be inferred from the list of physical constants given in Table 1. The principal contributions to bonding between Cu(II) and any of the ligands discussed here are going to come from ion−dipole and ion−induced dipole interactions. The stabilization energy gained from these terms will counteract any tendency to charge transfer as a consequence of the large difference in ionization energy between Cu^+ and any of the ligands. Thus, most complexes are stable for one or more of the following reasons: (i) the ligand has a large dipole moment, e.g., acetone or acetonitrile; (ii) the ligand has a high polarizability, e.g., pyrazine or 2-pentanone; (iii) the ligand has a high ionization energy, which then reduces the necessity for condition i and/or ii; a good example of this is carbon dioxide. Unfortunately, NO fulfils none of these criteria and, therefore, not unexpectedly the molecule is unable to form stable complexes with Cu(II). A more quantitative analysis that compares the interactions between copper(II), silver(II), and gold(II) with a range of ligands is in preparation.[64]

Conclusion

It has been shown that the pick-up technique can be used to prepare a wide selection of Cu(II) complexes, ranging from those containing more traditional ligands, such as pyridine, through to less familiar ligands, such as carbon dioxide. In many instances, the most stable (intense) $[Cu{\cdot}L_n]^{2+}$ combination corresponded to $I_{max} = 4$, an observation that can be attributed to a square planar arrangement of ligands with the two axial sites destabilized through Jahn−Teller distortion. For all the examples where $I_{max} > 4$, it has been possible to identify a common element in the form of an extended network of hydrogen bonds. Likewise, when $I_{max} = 2$, it appears to signify a marked change in the pattern of coordination, to either a bidentate ligand or some form of π complex.

The collisional activation of size-selected complexes resulted in several different modes of decay, ranging from the loss of neutral ligands through to charge transfer and the promotion of chemical reactions with the ligands. In a number of instances, the pattern of decay was determined by the stability of the metal-containing fragment. In other examples, particularly those identified with stable structures, there was a marked reluctance for complexes to lose neutral ligands. Some of the complexes identified in Table 1 can now be prepared with sufficient intensity for spectroscopic experiments to be undertaken. Preliminary results have been presented elsewhere on UV transitions, and more recent work has focused on the visible spectroscopy of complexes.

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