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[Cu·(H₂O)_n]²⁺ Clusters: The First Evidence of Aqueous Cu(II) in the Gas Phase

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Received July 7, 1997

It has often been said of clusters that they should be expected to form a bridge between isolated gas-phase species and the condensed phase,¹ and for singly charged metal ions there is strong evidence to support this claim.^{2,3} The wealth of information recorded over the past 20 years clearly demonstrates that quantities, such as condensed phase hydration enthalpies, can be reproduced from thermodynamic measurements made on gas-phase clusters consisting of metal ions and small numbers (~6) of water molecules.^{2,3}

Unfortunately, many of the more important metal ions in condensed phase chemistry and biochemistry are doubly charged,^{4,5} and for these there is very little data analogous to that recorded for singly charged metal ions. In solution, multiply charged metal ions are frequently expressed in the form of a complex between solvent and ion (for example, [Cu(H₂O)₆]²⁺ or [Ni(NH₃)₆]²⁺).⁴ Such units acknowledge an implicit relationship between ion and solvent, whereby it is recognized that isolated metal ions such as Cu²⁺ could not co-exist in the presence of single solvent molecules. Any consideration of the difference between the second ionization energy (IE) of a typical transition metal and the first IE of an organic solvent will immediately show that charge transfer should take place on contact.⁶ In an earlier study that involved using electrospray to generate multiply charged metal complexes, Kebarle and co-workers^{7–9} were unable to observe any [Cu·(H₂O)_n]²⁺ complexes in the gas phase, and concluded that it might take at least 15 water molecules to stabilize such a unit.^{7–9} Several groups have recently demonstrated the capability of electrospray as a method for producing multiply charged metal–ligand complexes from ions already in solution.^{7–12}

We have recently developed an alternative approach that appears capable of generating multiply charged metals ions in association with a broad range of solvent clusters.^{13–16} The technique relies on first producing neutral M·X_n complexes between metal (M) and solvent (X), and these are then ionized

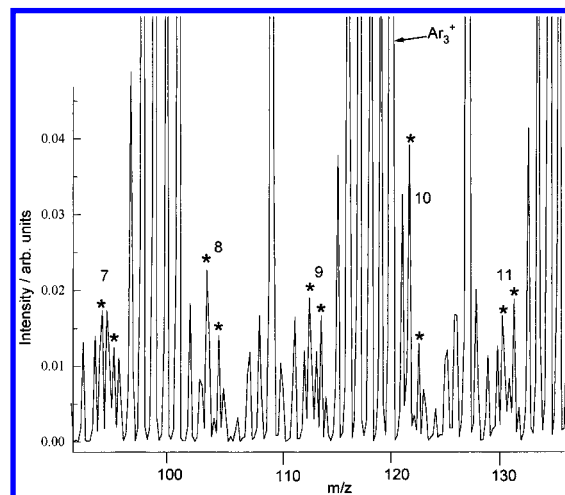


Figure 1. Section of a mass spectrum recorded following the “pick-up” of copper atoms by a cluster beam consisting of mixed water/argon clusters. The peaks identified as being due to [Cu·(H₂O)_n]²⁺ clusters are labeled in pairs with an asterisk and are due to the presence of ⁶³Cu and ⁶⁵Cu. Also shown is Ar₃⁺, which was used as a mass marker.

by electron impact to produce a doubly charged ion that is stable by virtue of the solvent environment surrounding the metal. To date the technique has been restricted to metals which can exert significant vapor pressures at or below 800 °C, i.e. magnesium^{12–15} and strontium.¹⁶ Reported here is what we believe to be a very significant step forward, in that the technique has now been extended to provide for the generation and study of multiply charged transition metal complexes. We present preliminary results for the series [Cu·(H₂O)_n]²⁺, which from the preceding discussion could be considered as one of the most difficult combinations to produce in the gas phase.

Copper vapor was generated by using a commercial Knudsen effusion cell operating at 1350 °C, which resulted in a partial pressure of metal atoms of between 10^{–3} and 10^{–2} Torr immediately above the cell. This region was crossed with a molecular beam consisting of mixed H₂O/Ar clusters, which resulted in the attachment of single metal atoms. Approximately 50 cm downstream the clusters entered the ion source of a high-resolution, double-focusing mass spectrometer (VG ZAB-E) where they were ionized by 100 eV electron impact. Figure 1 shows a short section of a mass spectrum recorded with the oven in operation. Since the beam entering the ion source consists predominantly of water and water/argon clusters, the corresponding ions dominate the mass spectrum. In addition, a significant contribution to the background signal originates from de-gassing by the oven and copper sample. However, the use of a shutter at the entrance to the oven makes it possible to confirm the presence of those copper-containing clusters highlighted in Figure 1. It is clear from the mass spectrum that the relative intensities of [Cu·(H₂O)_n]²⁺ ions do not always follow the established isotope ratio (*m/z* 63:*m/z* 65 = 2:1), and this is because both peaks are influenced by underlying ions with similar nominal masses. Although weak in comparison to its immediate neighbors, the ion signal for [Cu·(H₂O)₈]²⁺ is estimated to be approximately 10^{–11} A, which is sufficient for collisional fragmentation studies (see below) and spectroscopic measurements.¹⁷ Other Cu(II) complexes have been observed with intensities at least an order of magnitude larger than those recorded for [Cu·(H₂O)₈]²⁺.¹⁷

Figure 2 shows a plot of the relative intensities of [Cu·(H₂O)_n]²⁺ clusters as a function of *n*. Measurements were based on differences with the shutter open and closed and were made on both the ⁶³Cu and ⁶⁵Cu isotopes with the data being presented

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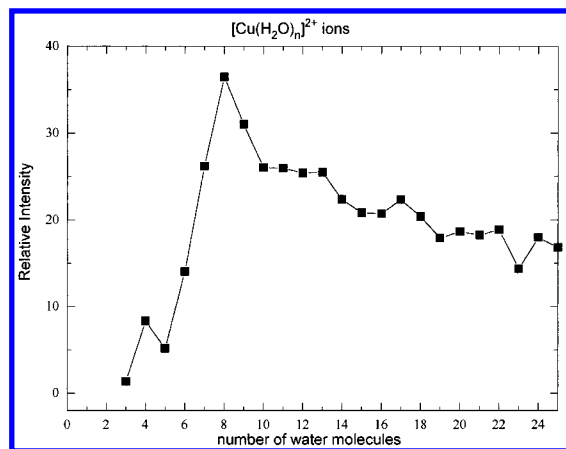


Figure 2. Relative intensities of $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ cluster ions plotted as a function of n . Each point is a weighted average of measurements made on the ^{63}Cu and ^{65}Cu isotopes, and background contributions were removed by taking the difference between the oven shutter open and closed.

as a weighted average of the two results. The shape of the distribution is due to a combination of two factors: (i) the instability of smaller clusters with respect to charge transfer and (ii) the natural decline in intensity that accompanies most cluster distributions as a function of increasing size. The slight discontinuity at $n = 4$ suggests the presence of a stable structure, and of related interest is the observation that $[\text{Cu}(\text{acetone})_4]^{2+}$ is at least a factor of 2 more intense than its immediate neighbors.¹⁷ No similar discontinuity is seen at $n = 6$, which is not too surprising since d^9 Cu(II) with octahedral coordination is known to be Jahn–Teller distorted, and the binding energies of the fifth and sixth ligands are lower than those of the other four.⁴ Cu(II) with 4-fold coordination can also undergo Jahn–Teller distortion, but it could take the form of an angular rather than radial displacement, which would not necessarily influence bond energies.⁴

Although $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is often quoted as the form adopted by aqueous Cu(II),⁴ the data in Figure 2 would imply that $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ is the more favorable primary solvation unit; however, there is a possibility that this particular combination may stand out simply because of an interplay between those factors which contribute to the shape of the profile. In many of the other doubly charged systems studied thus far, it has often been possible to equate intensity maxima with solvent shell development.^{13–16,19} In common with previous studies of Mg^{2+} and Na^+ in association with methanol,^{15,20} Figure 2 shows the presence of plateau regions, which in this case lie in the regions $n = 10–13$, $14–18$, and $19–22$. Such regions have been attributed to the presence of equivalent solvation sites, where molecules in the second shell are supported through strong hydrogen-bonding interactions with a highly orientated primary solvation shell.^{15,18} Since the hydrogen bond network in water should be more extensive and stronger than that seen in methanol, it is encouraging that Figure 2 reproduces previous patterns of behavior.^{15,18} The plateau region appears to embrace a total of 14 water molecules, and beyond $n = 22$ preliminary measurements show the trend to be sharply downwards. If we are assuming the primary solvation shell to consist of 8 water molecules then the total number of hydrogen bonding sites available to the secondary shell would be 16. Allowing for possible steric interactions, the numbers 8 and 14 for the primary and secondary solvation shells, respectively, would fit quite well with the data shown in Figure 2.

Figure 3 shows the result of a MIKE (Mass-analyzed Ion Kinetic Energy) scan of the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion performed in the presence of 10^{-6} mbar of air as a collision gas. The ion

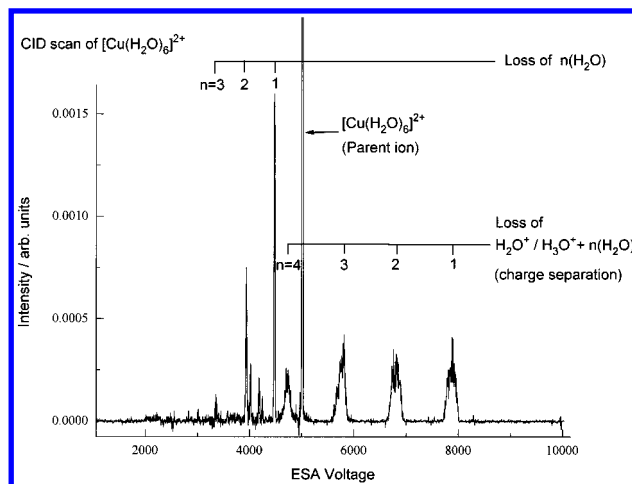
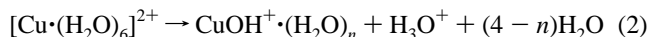
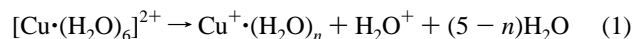


Figure 3. A MIKE scan recorded for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ with the mass spectrometer operating in the 2E mode.²³ The parent ion and peaks due to both the unimolecular loss of single water molecules and fragmentation accompanied by charge transfer are identified.

source was operated at 5 kV and the scan was performed in the 2E mode, which allowed for the transmission of ions with kinetic energies ≤ 10 keV.¹⁹ The parent ion appears at 5 keV, and any fragment ions observed at kinetic energies ≥ 5 keV are singly charged and formed as a result of Coulomb explosion induced by charge transfer. There are two principal contributions to the data shown in Figure 3: (1) unimolecular fragmentation of the parent ion via the loss of single water molecules (this step can be identified from the comparatively narrow peaks appearing below 5 keV; the loss of either one or two water molecules appears to be a favorable process; (2) collision-induced charge transfer followed by Coulomb explosion, which can be recognized from the broad peaks appearing both above and below 5 keV. An expansion of individual peaks shows them to be asymmetric and appearing to consist of two processes:



Since the water molecules are present in the complex as separate entities, it is assumed that they are lost as single molecules or ions and not as ionic clusters. Each reaction step will proceed via charge transfer to form H_2O^+ , which then either departs rapidly or first reacts with an adjacent water molecule. It is interesting to note that Coulomb explosion only begins with the loss of either $(\text{H}_2\text{O}^+ + \text{H}_2\text{O})$ or $(\text{H}_2\text{O} + \text{H}_3\text{O}^+)$, which would again support the idea of two water molecules being more weakly bound and probably occupying different sites from the remaining four molecules.

We have presented here the first results from a study of the properties of aqueous Cu(II) in the gas phase. The data show that the accepted primary solvation unit $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ does not exhibit any properties to suggest that it is particularly stable, but instead it appears to lose two water molecules quite readily. This pattern of behavior could be attributed to a Jahn–Teller distortion of the d^9 complex,⁴ which would result in a weakening of the binding energies of two ligands. By way of contrast, the complex $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ does appear to be more stable than its immediate neighbors, and the data also point to $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ as the preferred primary solvation unit.

Acknowledgment. The authors would like to thank the Royal Society and EPSRC for financial assistance and EPSRC for the award of a studentship to N.R.W.

JA9722436