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Collisional dissociation studies of $Cu^{2+}(H_2O)_n$ using electrospray ionization mass spectrometry

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Abstract

Contrary to an earlier report [A.T. Blades, P. Jayaweera, M.G. Ikonomou, P. Kebarle, J. Chem. Phys. 92 (1990) 5900], hydrated cupric ions $Cu^{2+}(H_2O)_n$ (n = 4–14) are readily produced in the gas phase by electrospray ionization and possess sufficient intensities for collision-assisted dissociation studies. Daughter ions, $Cu^{2+}(H_2O)_x$, with x as low as 2 are observed to be stable. Charge reduction yielding $CuOH(H_2O)^+_{n-y}$ is observed but declines in importance with increase in the size of the hydration shell. Methanol can exchange with some of the water molecules in $Cu^{2+}(H_2O)_n$. (Int J Mass Spectrom 185/186/187 (1999) 227–229) © 1999 Elsevier Science B.V.

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The cupric ion is a very important ion in biological systems that has received much study in the condensed phase. Gas phase studies of Cu^{2+} and other multiply charged metal cations have been very limited because the second ionization potentials of most metals are higher than those of potential ligands and the interaction of M^{n+} with a single such molecule results in electron transfer and reduction rather than association. However, the advent of electrospray ionization has enabled experimentalists to obtain ions solvated by several molecules relatively easily in the gas phase. Indeed, one of the necessary steps in the use of electrospray ionization in analytical chemistry is a desolvation to obtain the required bare ion.

Pioneering experiments by Kebarle and co-workers [1–4] showed that solvated, multiply charged metal ions, both main group and transition, can be transferred from solution to the gas phase with the use of electrospray ionization. They also observed that the solvated ions were far more stable with ligands such as DMSO and DMF than with water [1] for example, when $Cu^{2+}L_3$ (L = DMSO or DMF) was observed, no Cu^{2+} $(H_2O)_n$ could be created. It was surmised that because of the relatively high second ionization energy of copper, the ion would not be stable in the gas phase because of the observed charge reduction to $Cu^{2+}OH(H_2O)_m$ until the solvation shell contained more than 15 water molecules. Facile charge reduction of any $Cu^{2+}(H_2O)_n$ ions produced was thought to have occurred either during their escape from the droplets or in their passage through the desolvation chamber.

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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Proof that $Cu^{2+}(H_2O)_n$ with very small n ($n \geq 3$) is stable in the gas phase has been produced by a technique other than electrospray ionization [5]. Copper vapour from a Knudsen cell was allowed to interact with a molecular beam of mixed H_2O/Ar clusters which resulted in the pick-up of the metal atoms. The copper-containing clusters were subsequently ionized by electron impact in the ion source of a double-focusing mass spectrometer. The resulting mass spectra were dominated by H_2O/Ar cluster ions and background ions, but $Cu^{2+}(H_2O)_n$ ions with n from 3–24 were identified and some of the ions were present in sufficient intensities to be studied by MIKES (mass-analyzed ion kinetic energy spectroscopy).

Because $Cu^{2+}(H_2O)_n$ has proven to be stable and because electrospray ionization is a simple and gentle means of forming hydrated metal ions, we considered it advantageous to reexamine aqueous solutions of Cu(II) salts by this technique. Although initial studies showed the absence of $Cu^{2+}(H_2O)_n$ [6], we now attribute this observation to the presence of competing ligands; in particular, trace amounts of adventitious acetonitrile and acetone, which bind much more strongly to Cu^{2+} than water, were present due to previous experiments. We now find that $Cu^{2+}(H_2O)_n$ ions ($n = 4$–≥ 16) are readily formed by electrospray ionization and with sufficient intensities for collision–assisted dissociation (CAD) studies. The experiments were carried out using a quadrupole/hexapole/quadrupole instrument (VG Quattro) with an electrospray source fed by a syringe pump at a flow rate of 0.3 mL h^{-1} of a solution of an inorganic cupric salt. The required ions could be observed with a capillary potential in the range 2–3 kV. CAD spectra were obtained at a centre of mass collision energy of 9.0 eV using argon as collision gas at a pressure of 1×10^{-3} Torr. All copper-containing product ions were identified by comparison of the differences in mass-to-charge ratio between spectra of the hydrates of the ^{63}Cu and ^{65}Cu isotopes.

A typical spectrum obtained using a 10^{-3} M aqueous solution of $CuSO_4$ is shown in Fig. 1. The two major peaks are due to the hydrated proton: $(H_2O)_3H^+$ (m/z 55) and $(H_2O)_4H^+$ (m/z 73). The copper-containing peaks, $CuOH(H_2O)_n^+$, the results of charge reduction, are identified by their separation of 2 m/z units, in contrast to the 1 m/z unit separation for $Cu^{2+}(H_2O)_n$, and their 7:3 ratio of intensities because of the two isotopes of copper. These ions are of lower intensity than the $Cu^{2+}(H_2O)_n$ ions with $n =$ 8 and 9. A maximum in intensity at $n = 8$ was also found by Stace and co-workers [5], however, the pattern of $Cu^{2+}(H_2O)_n$ intensities and their intensities relative to those of $CuOH(H_2O)_n^+$ in our experiments could be varied by changes in the electric fields in the low pressure, interface region of the source. A "high" field in this region lead to $Cu^{2+}(H_2O)_n^+$ with smaller n and higher relative intensities of the charge-reduced $CuOH(H_2O)_n^+$. With a field of 40 V cm^{-1} no $Cu^{2+}(H_2O)_n$ was observed. The spectrum shown in Fig. 1 was obtained with no applied field. By a judicious selection of ion source conditions it was possible to obtain sufficient ion intensities of $Cu^{2+}(H_2O)_n$ ($n = 4$–14) for CAD studies. Shown in Fig. 2 are CAD spectra of $Cu^{2+}(H_2O)_n$ for $n = 4$, 8, and 11. The lower signal to noise ratios for $n = 4$ and 11 compared with that for $n = 8$ reflect the lower optimized intensities of these parent ions.

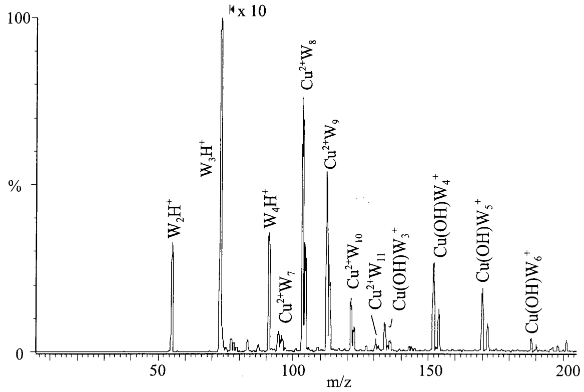

Fig. 1. Electrospray mass spectrum obtained for a 1.0×10 M solution of $CuSO_4$. W = H_2O.

Several generalizations may be made from this preliminary study regarding the stability of $Cu^{2+}(H_2O)_n$: (1) Low n ions are, as expected, the most stable towards collisional dissociation. Under the same CAD conditions 37% are dissociated for $n = 4$, 66% for $n = 8$, and 86% for $n = 11$, (2) The

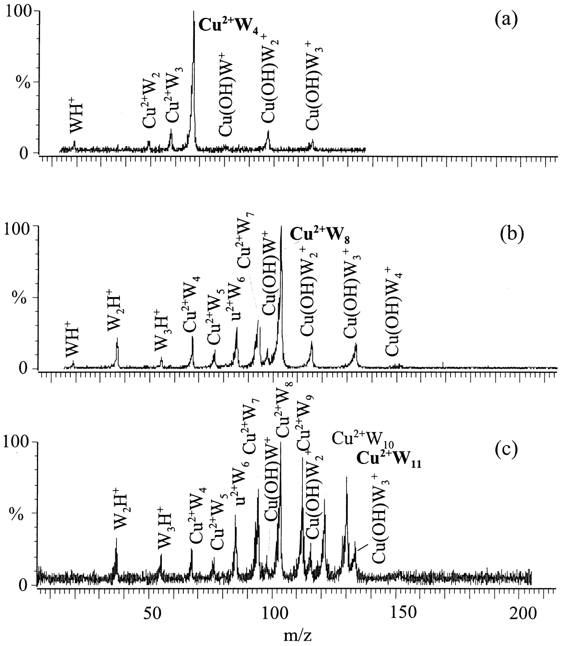

Fig. 2. CAD spectra for (a) $Cu^{2+}(H_2O)_4$, (b) $Cu^{2+}(H_2O)_8$, and (c) $Cu^{2+}(H_2O)_{11}$. Parent ions are in bold and printed horizontally. W = H_2O. Argon collision gas at a pressure of 1.0×10^{-3}; center of mass collision energy = 9.0 eV.

proportion of charge-reduced product ions decreases with increased solvation of the parent. However, even for the tetrahydrate, loss of water with no charge reduction is of equal probability to charge reduction. Both $Cu^{2+}(H_2O)_3$ and $Cu^{2+}(H_2O)_2$ are seen as stable products in Fig. 2(a), (3) $Cu^{2+}(H_2O)_8$ does appear to be a particularly stable ion, as previously suggested [5], (4) $Cu^{2+}(H_2O)_5$ is apparently less stable than $Cu^{2+}(H_2O)_4$ because the relative intensity of the latter is greater both for CAD and mass spectra, (5) charge reduction forming $CuOH(H_2O)_n^+$ is accompanied by the formation of $(H_2O)_mH^+$. The value of m increases as the degree of hydration of the parent ion increases, from 1 for $Cu^{2+}(H_2O)_4$ to a maximum value of 3 for higher hydrates. $(H_2O)_4H^+$ was never observed, (6) the tetracoordination in $CuOH(H_2O)_3^+$ appears to be a very stable configuration and may constitute a closed shell since $CuOH(H_2O)_4^+$ always has very low intensity regardless of the degree of hydration of the parent ion.

The failure of an initial attempt [1] to observe the production of $Cu^{2+}(H_2O)_n$ in an electrospray source must be attributed to the use of unsuitable experimental conditions. Such ions appear to be no less stable than other hydrated, doubly charged metal cations. Indeed, electrospray ionization is a convenient way of producing such ions in mass spectra which are almost free of interfering peaks. It may also be possible to produce $BeOH(H_2O)_n^+$, which was also suggested to be unstable with respect to charge reduction if n is less than 15. The smaller Be^{2+} is, however, probably more favorable to charge reduction in reaction with a hydration shell than is Cu^{2+}. Theoretical calculations predict that hydrated Be^{2+} has a first hydration shell containing four water molecules bound with a total energy of 384.4 kJ mol^{-1} [7].

Electrospray ionization is a convenient method of producing hydrated metal cations and hence enables their study at low collision energies with reactive gases in a collision cell [6,8]. We find, for example, that $Cu^{2+}(H_2O)_8$ will react with CD_3OH by both exchange–giving $Cu^{2+}(H_2O)_{8-x}(CD_3OH)_y$ where $x = 1$ or 2 and $y = 1$, 2, or 3, and by charge reduction–giving (mainly) $CuOH(H_2O)_{n-x}^+$ and $(H_2O)(CD_3OH)_aH^+$ $(a = 1 \ldots 3)$. These experiments are ongoing.

Acknowledgements

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