Ligand and H/D exchange of $Mn(H_2O)_6{}^{2+}$ and $Cu(OH)(H_2O)_4{}^{+}$ in the gas phase

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When ligand exchange of aqua complexes in the gas phase is examined by reaction with D_2O it is not accompanied by H/D exchange.

In solution, aqua complexes undergo exchange of intact ligands as well as proton exchange.[1] In the present work it is shown that whereas ligand exchange occurs in the gas phase, doubly charged aqueous complexes do not undergo proton exchange in the gas phase. Formation by electrospray of aqua complexes of doubly charged metal ions is well known.[2] However, only a few studies of ligand exchange in complexes of doubly charged metal ions in the gas phase have appeared.[3,4]

The spectra obtained when $Mn(H_2O)_6{}^{2+}$ is allowed to react with D_2O are shown in Fig. 1 for two different pressures of D_2O.[5] The parent ions occur at m/z 81.5 and the products of consecutive ligand exchange reactions occur at intervals of one m/z value above the parent ion. At low pressure the unexchanged reactant is the most abundant ion whereas the product of four ligand exchanges is the most abundant at high pressure. Since the ions are doubly charged, this shows that the exchange reaction leads to an increase in the mass of two Daltons. Hence the products have been formed by exchange of intact water molecules, and no evidence of hydrogen exchange is observed. The spectra shown in Fig. 1(*a*) and (*b*) include a group of peaks at m/z 72.5 and above which must arise from reactant ions which have lost one or more ligands. This is due to the poorly defined collision conditions when ion–molecule reactions (IMRs) are studied in a multipole. In order to optimize the yield of IMRs the

axial velocity of the ions is kept low, and under such circumstances the radial RF field in the multipole may contribute significantly to the kinetic energy which is available in the collisions.[6] When the pressure of D_2O is increased, products of addition as well as ligand exchange reactions are observed [Fig. 1(*b*)]. The six equidistant peaks above that from the reactant show that at this pressure all six water molecules in the parent ion can be exchanged. The abundance of the products formed by loss of a ligand is increased, and products of addition reactions are observed. In the observed addition products all the ligands have been exchanged. This phenomenon is well known from studies of H/D exchange reactions in quadrupole instruments.[7–10] Briefly it is a consequence of the instability of the addition product relative to dissociation back into the reactants. The addition product can be stabilized by different mechanisms but these all require a pressure at which all the ligands in the parent ion have been exchanged. For most of the aqueous complexes the largest clusters which we have observed under high-pressure conditions have nine water molecules, independently of the size of the parent complex.[11] This shows that the binding of a tenth ligand is very weak. A structure which is in agreement with this is shown in Scheme 1.

Scheme 1

Whereas H/D exchange has not been observed in the doubly charged ions, it is readily observed in singly charged ions. Fig. 2 shows the spectrum obtained when $^{63}Cu(OH)(H_2O)_4{}^{+}$ is allowed to react with D_2O. Such hydroxidoaqua complexes are

Fig. 1 Spectra obtained from the reaction between $Mn(H_2O)_6{}^{2+}$ and D_2O at two different pressures; (*a*) 0.20 (*b*) 0.40 mTorr. The reactant ion is indicated by *. The number at each group of peaks indicates the number of aqua ligands in the complex assigned to the peaks.

Fig. 2 Spectrum obtained from the reaction between $^{63}Cu(OH)(H_2O)_4{}^{+}$ and D_2O at 0.20 mTorr. The reactant ion is indicated by *. The number at each group of peaks indicates the number of ligands (including one hydroxido) in the complex assigned to the peaks.

Scheme 2

formed in the source along with the aqua complexes. The equivalent complex with manganese could not be generated in sufficiently high abundance to study its reactivity in IMRs. This difference in acidity of copper and manganese aqua complexes in the gas phase has been noticed before.[2] The reactant ion $^{63}Cu(OH)(H_2O)_4^+$ gives a peak at m/z 152, and the products of the exchange reaction are observed at intervals of one m/z value above. Products of exchange and ligand loss are observed at m/z 134 and above. The most abundant products occur at m/z 154 and m/z 156. This seems to indicate that exchange of the intact ligand is preferred for the singly charged complex, but the observation of peaks at m/z 153, 155, 157 shows that in the singly charged complex the hydrogen atoms can be exchanged one at a time.

The absence of H/D exchange in the reaction between the doubly charged complex $Mn(H_2O)_6^{2+}$ and D_2O is in agreement with the model which previously has been used to rationalize the reactivity of ligated doubly charged metal ions and of doubly charged molecular ions.[12–14] Excluding exchange of hydrogen radicals or simultaneous exchange reactions, the mechanism giving exchange of a singly hydrogen would have to proceed by intermediates in which the two charges are partially separated. The overall product of the reaction will be proton transfer rather than exchange as is observed at high D_2O pressures. A possible mechanism is shown in Scheme 2.

Protonation of inner-sphere ligands has been proposed to play a role in the exchange of water complexes.[15] However, in the gas phase formation of ions such as **1b** must be energetically disfavoured.[12,13] The absence of H/D exchange indicates that when an intermediate such as **1b** is formed in an IMR, the electrostatic repulsion prevents the incipient hydroxonium ion and the complex from remaining together for long enough for back exchange of a deuteron to occur. The overall outcome of the reaction will then be transfer of a proton rather than H/D exchange.

The structure of hydrated doubly charged metal ions and the dynamics of the exchange reaction are being very actively studied both experimentally and theoretically.[16–19] In aqueous solutions of $Mn(H_2O)_6^{2+}$ ligand exchange is faster than proton exchange.[20] The results presented here show that the exchange of the intact ligand has its parallel in the gas phase, but that the very different influence of electrostatic interactions prevents the occurrence of H/D exchange reactions.

Notes and References

1 J. Burgess, *Metal ions in solution,* Ellis Horwood, Chichester, 1978.
2 A. T. Blades, P. Jayaweera, M. G. Ikonomou and P. Kebarle, *J. Chem. Phys.*, 1990, **92**, 5900.
3 Y. D. Hill, B. S. Freiser and C. W. Bauschlicher, *J. Am. Chem. Soc.*, 1991, **113**, 1507.
4 U. N. Andersen and G. Bojesen, *Int. J. Mass Spectrom. Ion Process*, 1996, **153**, 1.
5 The experiments were carried out with a Finnigan TSQ700 tripelquadrupole instrument in which the collision region is in fact an octapole. The complexes were generated by electrospray ionization from 0.20 mm aqueous solutions of appropriate salts, and the ion–molecule reactions were conducted as described in ref. 4.
6 K. M. Ervin and P. B. Armentrout, *J. Chem. Phys.*, 1985, **83**, 166.
7 N. N. Dookeran and A. G. Harrison, *J. Mass Spectrom.*, 1995, **30**, 666.
8 J. A. Stone, *Org. Mass Spectrom.*, 1993, **28**, 1119.
9 N. N. Dookeran and A. G. Harrison, *J. Am. Soc. Mass Spectrom.*, 1994, **6**, 19.
10 A. Ranasinghe, R. G. Cooks and S. K. Sethi, *Org. Mass Spectrom.*, 1992, **27**, 77.
11 S. B. Nielsen and G. Bojesen, unpublished work.
12 R. Tonkyn and J. C. Weisshaar, *J. Am. Chem. Soc.*, 1986, **108**, 7128.
13 L. M. Roth and B. S. Freiser, *Mass Spectrom. Rev.*, 1991, **10**, 303.
14 S. D. Price, M. Manning and S. R. Leone, *J. Am. Chem. Soc.*, 1994, **116**, 8673.
15 T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, 1966, **5**, 1100.
16 R. Åkesson, L. G. M. Pettersson, M. Sandström and U. Wahlgren, *J. Am. Chem. Soc.*, 1994, **116**, 8705.
17 A. K. Katz, J. P. Glusker, S. A. Beebe and C. W. Bock, *J. Am. Chem. Soc.*, 1996, **118**, 5752.
18 F. P. Rotzinger, *J. Am. Chem. Soc.*, 1997, **119**, 5230.
19 E. D. Glendening and D. Feller, *J. Phys. Chem.*, 1996, **100**, 4790.
20 T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.