



Cluster-to-metal electron transfer in $[\text{Mn} \cdot (\text{pyridine})_n]^{2+}$ complexes

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Received 15 June 2000; in final form 11 September 2000

Abstract

Experiments on the collisional activation of $[\text{Mn} \cdot (\text{pyridine})_n]^{2+}$ have revealed the presence of a new charge transfer channel, whereby clusters of the form $(\text{pyridine})_k^+$ for $k \leq 3$ are observed when $n \leq 6$. Several possible metal–ligand configurations are considered including sandwich and charged-separated structures. It is concluded that the complexes consist of a central doubly charged metal ion, and that electron transfer from a molecule is accompanied by the simultaneous association and removal of nearest neighbour ligands. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Recent experiments on the chemistry of gas-phase metal ions have sought to prepare complexes where the metal ion occupies a more commonly occurring oxidation state, e.g., Cu(II), Mg(II), etc. [1–11]. As a consequence of the high charge state, the variety of chemical processes that can be promoted within such complexes, either by collisional or laser excitation, increases dramatically with charge transfer featuring quite prominently [1–3,7–9]. In most instances, the direction of electron movement is interpreted as being from a single ligand (molecule) to the metal ion (LMCT); a picture that has been taken from the very extensive volume of work undertaken on charge transfer in the condensed phase [12]. Far fewer examples of metal ion–ligand charge transfer (MLCT) have been documented in the gas phase

[10,11]; but again these follow a pattern established from studies of similar systems in the condensed phase.

Reported here are the results of an experiment where unambiguous evidence is provided of cluster–metal charge transfer (CMCT). A section of the shell of molecules surrounding a doubly charged metal ion appears to co-operate in the process of charge transfer, and then separate from the singly charged metal ion as a single unit. Such a process could have implications for the interpretation of LMCT reactions in the condensed phase.

2. Experimental section

A detailed description of the general instrumentation used for generation, resolution and detection of the cluster beam has been provided in previous publications [7–9]. Briefly, argon carrier gas at a pressure of between 30 and 40 psi, was passed through a custom built reservoir containing

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pyridine in its liquid state. The resultant mixture of argon and pyridine vapour was then subjected to supersonic expansion through a conical nozzle, followed by collimation 2 cm downstream by a skimmer 1 mm in diameter. Midway between the expansion chamber and the mass spectrometer, the cluster beam passed over the mouth of a high temperature effusion cell (DCA Instruments, EC-40-63-21) equipped with a crucible of pyrolytic boron nitride, in which metal vapour was generated. The vapour was allowed to diffuse into the flight tube to create a region where it could interact with the cluster beam; earlier experiments using this type of 'pick-up' technique have shown that the presence of neutral clusters in the form of $\text{Ar}_n(\text{pyridine})_m$ is essential to the success of the method.

Signal intensities measured on the apparatus over a series of experiments have suggested that the optimal partial pressure of metal vapour is between 10^{-1} and 10^{-2} Torr. Above this pressure, disruption of the cluster beam results in reduced signal intensity, and at lower pressures the metal/solvent clusters signal decreases. For manganese, the above partial pressure was estimated from the observation that the effusion cell operated most effectively when the temperature was held at 1100°C , as measured with a standard C-type thermocouple. A shutter at the exit of the effusion cell was used to confirm the identity of clusters containing manganese.

The neutral manganese/pyridine clusters were ionised by 100 eV electrons within the ion source of a high resolution, double focusing mass spectrometer (VG ZAB-E), and were then accelerated by a potential of +5 kV. After passing through a field free region, ions were selected according to their mass/charge ratio in a magnetic sector. When referenced to the mass increment separating singly charged ions, doubly charged species appeared in the mass spectra at half integer intervals. A second field free region separated the magnetic sector from an electrostatic analyser (ESA), and the presence of a gas cell in this region permitted the collisional activation of size-selected parent ions. For the complexes discussed here, fragmentation processes were examined in the presence of $\sim 10^{-6}$ mbar of air as a collision gas, and product ions

(singly and doubly charged) arising from CID were identified by scanning the ESA in the form of mass-analysed ion kinetic energy (MIKE) scans [13]. These scans were performed on selected doubly charged ions with kinetic energies of 10 keV, and provided straightforward detection and verification of fragment ions resulting from unimolecular decay and Coulomb explosion. Final ion detection took place at a Daly detector, where phase sensitive detection was facilitated by a Stanford Research Systems SR850 lock-in amplifier.

3. Results and discussion

Fig. 1 shows a plot of the relative intensities of $[\text{Mn} \cdot (\text{pyridine})_n]^{2+}$ ions as a function of size, n . The overall shape of the distribution is very similar to that recorded for many doubly charged metal–ligand complexes [7–9,14,15], and its profile is influenced by a number of 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 followed by Coulomb explosion. The ionisation energy of Mn^+ is 15.64 eV, compared with that of pyridine at 9.25 eV, 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 stability. Particularly stable metal–ligand combinations are associated with high ion intensities, and it has recently been shown that large $[\text{M} \cdot \text{L}_n]^{2+}$ complexes will preferentially fragment down to a stable structure [16]. Finally, the decline in intensity seen for larger ions is a characteristic feature of cluster experiments in general. As Fig. 1 shows, for most $[\text{M} \cdot \text{L}_n]^{2+}$ systems it is possible to identify a minimum stable size, $[\text{Mn} \cdot (\text{pyridine})_2]^{2+}$, and the most stable combination, which in this case is $[\text{Mn} \cdot (\text{pyridine})_4]^{2+}$.

Fig. 2 shows three examples of MIKE spectra recorded following the collisional excitation of size-selected $[\text{Mn} \cdot (\text{pyridine})_n]^{2+}$ complexes at $n = 3, 4$, and 6. As a general observation embracing a wide range of systems studied thus far [7–9,14,16], it would appear that decay via

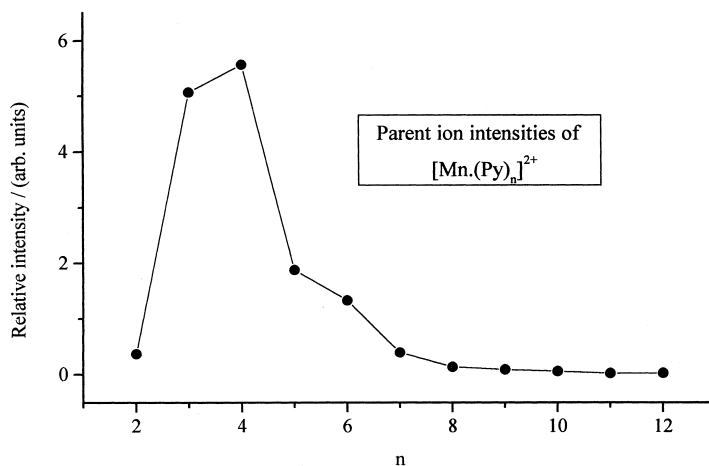


Fig. 1. Distribution of relative intensities recorded for $[\text{Mn} \cdot (\text{pyridine})_n]^{2+}$ cluster ions plotted as a function of n .

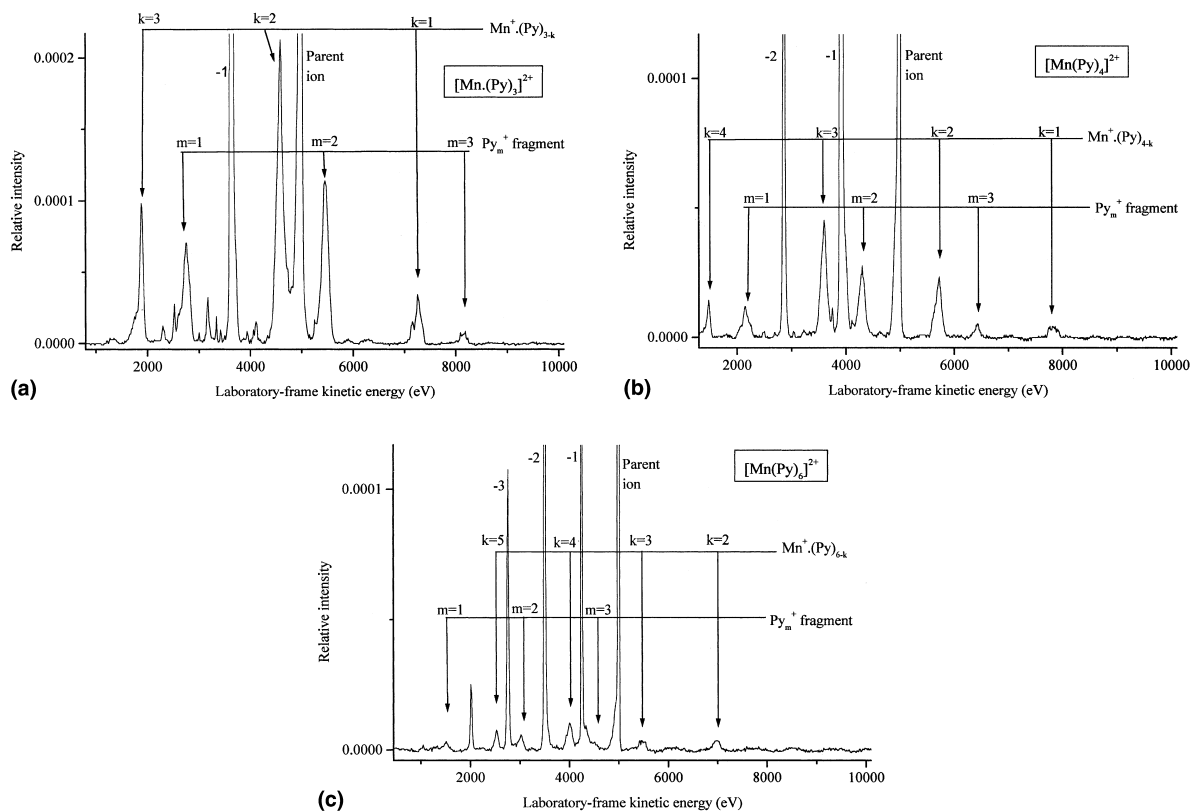
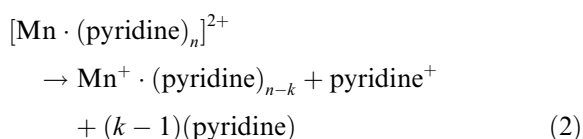
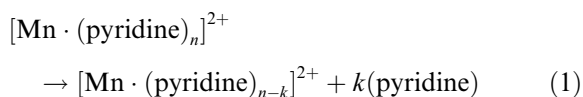


Fig. 2. Fragment ion kinetic energy spectra recorded following the collisional activation of size-selected $[\text{Mn} \cdot (\text{pyridine})_n]^{2+}$ ions: (a) $[\text{Mn} \cdot (\text{pyridine})_3]^{2+}$; (b) $[\text{Mn} \cdot (\text{pyridine})_4]^{2+}$; (c) $[\text{Mn} \cdot (\text{pyridine})_6]^{2+}$. The terms -1 , -2 , and -3 denote, respectively, the loss of one, two, and three neutral pyridine molecules.

collisional activation is dominated by two quite distinct processes: (i) the unimolecular loss of neutral ligands; a process that becomes more probable as the complexes increase in size; (ii) charge transfer to a single molecule, but frequently accompanied by the additional loss of neutral molecules. This process becomes less probable as a function of size. These two steps can be summarised as follows:

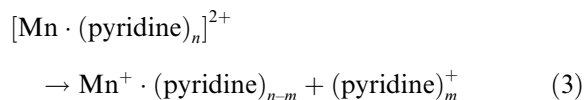


Features due to charge transfer are clearly distinguished by their width, which arises from the release of kinetic energy as a result of Coulomb repulsion between the separating singly charged fragments. This broadening also leads to a loss of resolution, which on a double-focusing instrument operating in the MIKE mode can prevent the accurate assignment of reaction products involving the addition or loss of a proton.

Whilst unimolecular decay is an expected outcome following internal excitation, the route to charge transfer is less obvious. Two possible mechanisms have been proposed previously: (i) a complex undergoes unimolecular decay until it reaches the minimum size identified for that particular system, further fragmentation would then render the ion unstable and LMCT could take place. However, since charge transfer is seen following the loss of just two ligands from $[\text{Mn} \cdot (\text{pyridine})_6]^{2+}$ (Fig. 2c), as far as these larger complexes are concerned the data presented here would not appear to support such a proposal. It is, however, quite possible that a mechanism such as this may operate in the small ($n \leq 3$) complexes. (ii) An alternative proposal is that collisional activation promotes internal electronic excitation within a ligand, and this in turn facilitates LMCT. Evidence in support of such a mechanism has been found recently in a laser study of small $[\text{Ag} \cdot (\text{pyridine})_n]^{2+}$ complexes [16]. Following the electronic excitation ($\pi \leftarrow \pi^*$) of a pyridine mole-

cule in the first solvation shell at UV wavelengths, LMCT was observed to be the dominant decay mechanism. Therefore, by analogy with photoexcitation, collisional activation could promote LMCT if the collision partner has access to molecules in the first solvation shell, which then undergo electronic excitation. Such a mechanism would account for the observed size effect, since molecules in the first solvation shell would be shielded by additional solvation.

In addition to the two processes identified above, it is quite clear from Fig. 2 that a second type of charge transfer process, which had not been recognised previously, is operating in small $[\text{Mn} \cdot (\text{pyridine})_n]^{2+}$ complexes. This new process can be summarised as follows:



and leads to the appearance of pyridine cluster ions. For $m = 1$, the ion identified is complementary to reaction (2) above, and this type of product has been seen both by ourselves [7] and Kebarle and co-workers [1–4], in several earlier studies of multiply charged systems. In addition, weak features arising from the loss of $(\text{ROH})_{2,3}\text{H}^+$ ($\text{R} = \text{H}, \text{CH}_3, \text{and } \text{C}_2\text{H}_5$) have also been observed following the collisional excitation of complexes where hydrogen-bonding makes a significant contribution to the development of solvent structure [17,18]. These latter units could be viewed as integral components of the solvent lattice. In contrast, the products in reaction (3) corresponding to $k = 2$ and the above represent the appearance of pyridine cluster ions, which from their intensities would suggest that this process represents a significant charge transfer route. What is particularly interesting about this observation is that prior to charge transfer, the individual pyridine molecules would not be expected to be in the form of a cluster. In the solid state, the geometry of a $[\text{Mn} \cdot \text{L}_4]^{2+}$ complex is either tetrahedral or square with minimal contact between ligand molecules [19], and for $[\text{Mn} \cdot (\text{pyridine})_3]^{2+}$ the separation between molecules should be even greater. Although the intensity of $[\text{Mn} \cdot (\text{pyridine})_2]^{2+}$ is significantly lower than that of the examples

given above (see Fig. 1), weak features due to the loss of pyridine⁺ and (pyridine)₂⁺ could be seen following collisional activation. The above observations could easily be accommodated within structures which match the solid-state data, where the Mn(II)/pyridine complexes consist of a central metal ion to which pyridine rings are co-ordinated via their nitrogen atoms, and where the charge on the metal ion is stabilised via back-bonding [19].

However, in the less rigid environment of the gas phase it is quite possible that alternative geometries become significant in the development of structure, and that one or more of these could be responsible for our observations. Nevertheless, the selection of any new structure, which departs from the established solid-state configuration, has to be consistent with the two other fragmentation pathways observed for this ion series. There are two realistic alternatives to that of a solvated double charged metal ion. The ions being studied could possibly consist of two singly charged components of the form Mn⁺–(pyridine)_n⁺. This type of complex would offer the obvious advantage of being able to fragment in a manner suggested by reaction (3). The interactions responsible for stability (ion–dipole and ion–induced dipole) would be similar to those present in the [Mn · (pyridine)_n]²⁺ units, but weaker because the ions are singly charged and because there will also exist a strong repulsion between the two like charges. Multiply charged ions of this form are known to exist for many atomic and molecular clusters and their pattern of fragmentation is well documented [20]. However, the stability of these ions frequently requires the presence of large numbers of intervening molecules in order to moderate the repulsion between the two positive charges. A useful comparison could be made with benzene, which is probably the system closest to pyridine where reliable data exist. The minimum size of benzene cluster capable of supporting two separate positive charges is (C₆H₆)₂₃²⁺ [20]. Following collisional activation, these ions undergo Coulomb explosion to exhibit a very broad range of singly charged fragments. Within the context of the results presented in Fig. 2, an ion with the structure Mn⁺–(pyridine)_n⁺ might have been ex-

pected to exhibit (pyridine)_k⁺ fragments up to $k = 6$. In contrast, all of the data recorded show that k is always ≤ 3 , which suggests that the ions are generated by the clustering of neighbouring molecules surrounding Mn²⁺.

An alternative arrangement to that proposed above, is one where the pyridine molecules remain neutral, but are stacked above and/or below the metal ion in the form of a sandwich structure. Clusters of this type have been identified previously for metal ions, such as Ti⁺ and V⁺; but have been shown to evolve in a sequence of the form M_n⁺(benzene)_m, where $m = n + 1$ [21,22]. For our examples we require $n = 1$, but $m = 2–6$. The observations of Yasuike et al. [21] are attributed to an interaction between the 3d orbitals of the metal and the π electrons of the benzene molecule. Two further observations are relevant: (i) the series for Cr⁺ (isoelectronic with Mn²⁺) stops at $n = 1$, $m = 2$ [21], and a very similar result has emerged from our own experiments on Cu²⁺, Ag²⁺ and Au²⁺ in association with benzene, where the only ion observed is [M · (C₆H₆)₂]²⁺ [9,17]. Comparable experiments involving Mn²⁺ showed the presence of [Mn · (C₆H₆)_n]²⁺ ions for $n \leq 6$, and although [Mn · (C₆H₆)₂]²⁺ has (C₆H₆)₂⁺ as one of its fragments, the equivalent fragment ion from the larger clusters, has a very low intensity [17]. The one common feature in all of these systems (including Mn²⁺) is that the ion [M · (C₆H₆)₂]²⁺ has the highest intensity and that beyond $n = 3$, the intensities decline rapidly. In contrast, the relative intensities of [Mn · (pyridine)_n]²⁺ clusters exhibit a pattern of behaviour which is identical to that seen in many other gas-phase examples where it is known from other sources, that one atom of each molecule (nitrogen in this case) is co-ordinated directly to the metal ion in the first solvation shell [8,9]. In contrast to the metal ion/benzene sandwich structures, the $n = 2$ manganese/pyridine complex has no significant intensity.

4. Conclusion

A new charge transfer route has been identified in small [Mn · (pyridine)_n]²⁺ complexes,

where following collisional activation the ion undergoes CMCT, with $(\text{pyridine})_3^+$ being the largest sized fragment observed. Based on accumulated evidence from other related complexes, it is proposed that the structures of the ions are of the form where molecules are co-ordinated to a central Mn^{2+} rather than in the form of sandwich structures. Under these circumstances, the results reported here correspond to charge transfer to a ligand, the loss of which is accompanied by association with and removal of one or two of its nearest neighbours. The circumstance which favours this process in Mn^{2+} but not in other pyridine-based complexes, such as $[\text{Cu} \cdot (\text{pyridine})_n]^{2+}$ or $[\text{Au} \cdot (\text{pyridine})_n]^{2+}$ [15,17], is the relatively low second ionisation energy of manganese. For other metals, such as copper or silver, where the second ionisation energies are much higher, the resultant large release of repulsive Coulomb energy is probably sufficient to break up any clusters which may be formed. An additional factor which may contribute to the effectiveness of the CMCT process is that clusters frequently have lower ionisation energies than single molecules. In the liquid state, where there may be a number of molecules in close proximity to the recipient of a charge transfer reaction, the reduced ionisation energy of a cluster of molecules could make a significant contribution to the efficiency of a LMCT process.

Acknowledgements

The authors would like to thank EPSRC for financial assistance and for the award of a studentship to GA-B.

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