Available online at www.sciencedirect.com
International Journal of Mass Spectrometry 249–250 (2006) 289–295
www.elsevier.com/locate/ijms

Gas phase studies of metal dimer complexes, $M_2L_n^+$, where M = Zn and Mn, and L = pyrrole and furan, for n in the range 1–5

Guohua Wu, Anthony J. Stace*

Department of Physical Chemistry, School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RH, UK

Received 11 October 2005; received in revised form 16 December 2005; accepted 16 December 2005
Available online 24 January 2006

Abstract

The combination of a pick-up technique and high resolution mass spectrometry have been used to prepare and study the fragmentation patterns of singly charged metal dimer complexes consisting of Zn_2 and Mn_2 in association with up to five molecules of either pyrrole or furan. The results of the fragmentation experiments are consistent with the picture that the metal dimers remain intact within the complexes, but that Zn_2 does not appear to carry a positive charge. Of the two molecules, furan appears to be less strongly bound than pyrrole to either metal dimer.

Keywords: Metal dimer; Zinc; Manganese; Pyrrole; Furan

1. Introduction

Gas phase organometallic ion chemistry has been the subject of intense research activity in recent years [1]. The chemical properties of complexes between transition metal cations and small organic ligands have attracted considerable interest over the past two decades, especially with respect to bond activation and other catalytic processes [2]. Their importance in biological structures and catalysis means that many studies have sought to understand the interaction of metal ions with π-electrons [3], which accounts for the extensive work that has been performed on the metal cation interactions with the benzene ligand. In contrasts, complexes between heterocyclic molecules and metal cations, have received only modest attention in the gas phase [4–9]. However, because of their importance in polymerization, in catalysis and in biomedical studies [10], quantitative data on such properties as binding energies are becoming available. Most notably, Dunbar and co-workers have investigated the binding energies and geometries for a number of main-group and transition-metal cations coordinated with pyrrole and furan complexes [7,8]; transition metals cations being the primary focus because of the link with catalysis [11,12]. Since the first step in heterogeneous catalysis involves the adsorption of one or more reactant molecules on to a surface [1,13], experimental and theoretical studies characterizing this interaction through the use of transition metal atoms, clusters and ions could provide valuable insight into the nature of the surface/molecular relationship [14].

In the work reported here we have examined the fragmentation patterns of the metal ion dimer complexes $Mn_2L_n^+$ and $Zn_2L_n^+$ (L = pyrrole and furan) for n in the range 1–5. These and related data are used to draw conclusions regarding the structures of the complexes and factors that influence the various competitive fragmentation pathways, and useful comparisons have been made with the work of Dunbar and co-workers [7,8], which is one of several experiments where metal cation–heterocylic binding energies have been measured [9,15,16]. In addition, Stöckigt has performed ab initio and density functional calculations on Al^+-furan and Al^+-pyrrole [6].

A number of papers over the past 20 years have examined the physical and chemical properties of Mn_2^+ [17–23]. Several groups have measured the bond dissociation energy, but unfortunately the data carry a wide discrepancy. Ervin et al. [17] derived D_0, as 0.85 ± 0.2 eV (82.3 kJ mol^{-1}) following collision-induced dissociation, whereas Jarrold et al. [18] arrived at a value for D_0, as 1.39 eV (134.8 kJ mol^{-1}) from a photodissociation study. Finally, Houriet and Vulpius [19] determined D_0 as 2.1 ± 0.3 eV (203 kJ mol^{-1}) from collisional activation experiments. In a very recent study, Terasaki et al. [20] assigned the electronic ground state of Mn_2^+ as $^{12}\Sigma_g^+$ with a bond length of 3.01 Å; however, Gutsev et al. [21,22] suggest the ground

---

* Corresponding author. Tel.: +44 1159513450.
E-mail address: tony.stace@nottingham.ac.uk (A.J. Stace).

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.12.014

state is $^{10}\Pi_u$ based on results from calculations using density functional theory; both the $^{12}\Sigma_g{}^+$ and $^{10}\Pi_u$ states are very close in energy. Support for the value obtained by Jarrold et al. [18] has come from observations on the reactivity of $Mn_2{}^+$ with a range of n-donor bases by Larsen et al. [23]. They showed that the reactivity of $Mn_2{}^+$ is frequently accompanied by dissociation of the metal–metal bond, and that the affinities of certain molecules for Mn^+ could be used to calibrate the $Mn_2{}^+$ bond energy.

Since atomic zinc has a closed-shell $3d^{10}4s^2$ configuration, only weak van der Waals interactions are expected between two ground-state atoms. Values of the Zn_2 binding energy range from 0.168 ± 0.025 eV, determined by Carlson and Kuschnir [24] to as low as 0.02 eV, as calculated by Gutsev et al. [22]. For the dimer cation, D_0 (Zn^+–Zn) has been estimated as 0.56 eV by Freiser et al. [25] using 0.168 ± 0.025 eV as D_0 (Zn–Zn) together with the ionization energies of the zinc atom and dimer. However, Gutsev et al. [22] obtained the much higher value of 1.73 eV from their calculations on $Zn_2{}^+$. Comparing Zn_2 with $Zn_2{}^+$, the latter bond energy is expected to be stronger, because removing a 4s electron from Zn_2 can lead to the formation of a single 4s + 4s bond in $Zn_2{}^+$. The binding energies of just a few zinc cation–ligand complexes have been measured [26–28] and although dimetallic complexes have received little attention in the gas phase, the first synthesis of a solid-state compound containing a zinc–zinc bond has been carried out recently by Resa et al. [29].

The work reported here represents one of the first CID studies concerned with the gas phase coordination of significant numbers of large molecules to a metal dimer, and we believe that that a qualitative picture of the structure of the metal–molecule complex can be inferred from the results.

2. Experimental

A detailed description of the instrumentation used for the generation, resolution and detection of metal-containing complexes has been previously given [30]. Briefly, argon carrier gas at a pressure of about 50 psi was passed through a custom built reservoir containing pyrrole or furan in its liquid state (for furan, argon was passed through at 60 psi), enabling molecules of the solvent to enter the argon flow. A mixture of argon and pyrrole or furan vapour was then subjected to supersonic expansion through a pulsed conical nozzle, followed by collimation 2 cm downstream by a 2 mm diameter skimmer. 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 composed of pyrolytic boron nitride, from which metal vapour was generated. Metal vapour was allowed to diffuse into the flight tube in order to create a region where the vapour and the cluster beam could interact. It is not clear that pyrolytic boron nitride is the best crucible material for manganese because the walls of the vessel exhibited considerable deterioration during an experimental period lasting two weeks.

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, scattering of the cluster beam results in reduced signal intensity, and at lower pressures the metal/solvent cluster signals are low due to fewer collisions. For manganese and zinc, the above partial pressure was estimated from the observation that the effusion cell operated most effectively when the temperature was held at 1150 °C and 400 °C, respectively, as measured with a standard C-type thermocouple. Formation of neutral metal atom and dimer/solvent clusters results from the collision of metal atoms with argon/solvent clusters, with the energy from the collision being dispersed by the ejection of argon atoms. A shutter at the exit of the effusion cell was used to confirm the identity of clusters containing manganese or zinc, and where a survey was performed of the relative intensities of parent ions of a given series, the difference was taken between the signal intensity with the shutter open and closed. This approach removed any contribution from background signal that was not dependent on material originating from the effusion cell.

The neutral metal/solvent 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 through 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. 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 many of the complexes discussed here, fragmentation processes were examined in two ways: (i) metastable decay promoted through residual internal energy remaining in the complexes after electron impact ionisation, and recorded in the absence of any collision gas (background pressure $\sim 10^{-8}$ mbar); (ii) collision-induced dissociation (CID) promoted through the presence of $\sim 10^{-6}$ mbar of air as a collision gas. Fragments arising from both processes were identified by scanning the ESA in the form of a mass-analysed ion kinetic energy (MIKE) scan. Final ion detection took place at a Daly detector, where a Stanford Research Systems SR850 lock-in amplifier facilitated phase sensitive detection. Pyrrole and furan were purchased from Aldrich Inc. in 98% purity and used without further purification.

3. Results and discussion

3.1. Bonding and the collision-induced fragmentation patterns of M_2L^+ complexes

Under the experimental condition described above, a series of metal–ligand ions, containing two metal atoms of the form, $M_2L_n{}^+$ (M = Zn, Mn; L = pyrrole, furan; n = 1–8), have been observed in the mass spectra. It is to be expected that the similar experimental conditions also give rise to a wide range of singly and doubly charged ions of the form $ML_n{}^+$ and $ML_n{}^{2+}$. However, the interest here is primarily in those ions containing two metal atoms in association with up to five molecules of either pyrrole or furan.

Complex ions of the form M_2L^+ were size-selected and subjected to collisional activation. Fig. 1 shows typical fragmentation patterns recorded for all four metal dimer–single

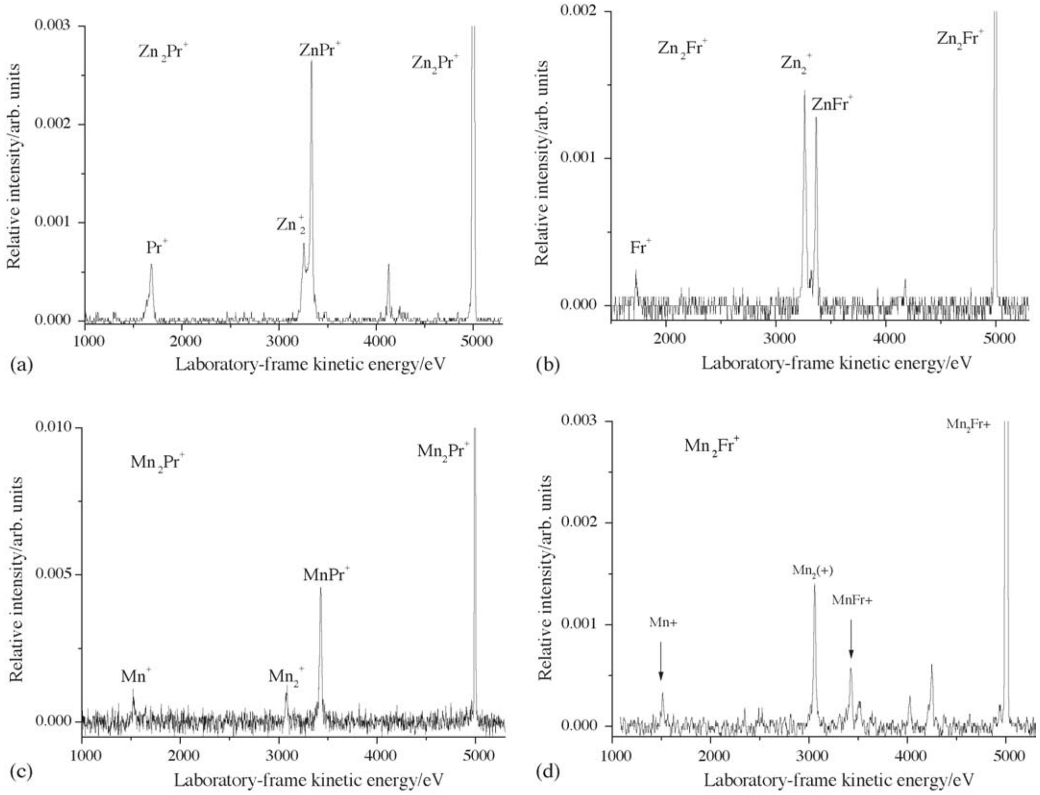

Fig. 1. Ion kinetic energy (MIKE) spectra recorded following the collisional activation of (a) Zn_2Pr^+, (b) Zn_2Fr^+, (c) Mn_2Pr^+ and (d) Mn_2Fr^+.

molecule M_2L^+ combinations. The observed fragmentation products cover the range ML^+, $M_2{}^+$, L^+ and M^+. The major product ions in the CID spectra of pyrrole-containing ions, M_2Pr^+ (Pr = pyrrole) are due to the loss of one neutral metal atom to give MPr^+; in contrast, binuclear metal $M_2{}^+$ ions, produced by the loss of an intact pyrrole molecule, are relatively small. No pathways involving the breaking of chemical bonds of ligands were observed in any of the experiments. With regard to the M_2Fr^+ (Fr = furan), MFr^+ and $M_2{}^+$ were the main fragments produced; however, in contrast to M_2Pr^+, they were of similar intensity. This differences may be related to differences in binding energy with respect to the loss of either a ligand or a metal atom from each M_2L^+ complex. For metal atom–ligand complexes, Nanayakkara and Freiser have studied bonding one and two pyrrole molecules to Co^+ by photodissociation threshold measurements [5], and Rodgers et al. [31] have applied threshold collision-induced dissociation to obtain the bond energies of a series of metal ions pyridine complexes. Results from this latter study show bond dissociation energies (BDE) involving Mn^+ to be the weakest of all of the first row transition metal ions. This low BDE can be attributed to the very stable $4s^1 3d^5$ electronic configuration of ground-state Mn^+ (^7S). Since both the 4s and 3dσ orbitals are occupied and high-spin coupled, the Pauli repulsion between the metal and any ligands is highest for Mn^+ complexes. Although pyrrole and furan were not among the ligands evaluated, similarities in structure with some of those studied, suggest that the binding energies between Mn^+ and either pyrrole or furan might be comparable. Gapeev et al. [7] have determined the binding energies of one and two pyrrole molecules to a number of transition metal cations, and more recently, Grimm et al. [8] have determined the binding energies of furan to both main-group and first-row transition metal series. The general trend appears to be that, of the transition metal ions surveyed, the binding energy to Mn^+ is, in both cases, the lowest. If the pattern of behavior seen for other molecules is followed, then the binding energies of furan and pyrrole should be slightly higher to Zn^+ than to Mn^+ [31]. If the same trend exists in the binuclear metal complexes Zn_2L^+ and Mn_2L^+, the ligand–metal bond energies for the manganese dimer ion should be smaller than the corresponding bond energies for the zinc dimer ion. In which case, there will be easier to lose a ligand molecule from Mn_2L^+ when compared with Zn_2L^+, which is qualitatively consistent with the results in Fig. 1.

Grimm et al. [8] have compared the binding energies of furan complexes with those of the corresponding benzene and pyrrole complexes across a series of ions consisting of first-row transition metals. The comparable pattern of binding energies of these three molecules suggests very similar electronic interactions, namely that furan is a π-bonding ligand closely parallel to benzene and pyrrole. However, the withdrawal of electron population from the π system by the electronegative oxygen heteroatom reduces the electrostatic contribution, and so binding is weaker to furan than to either benzene or pyrrole. Such a picture is again consistent with what is seen in Fig. 1, where the bare metal dimer fragment is comparatively abundant when furan is the ligand.

Table 1
Relevant ionization energies (eV)

Pyrrole	Furan	Zn	Mn	Zn_2	Mn_2
8.207	8.88	9.394	7.434	9.0	6.9

Aside from the dominant fragment ions that result from loss of a single ligand or metal atom, there are also present in Fig. 1 a series of weaker peaks that differ according to the nature of the complex. The fragments are Pr^+, Fr^+ from dissociation of the zinc complexes, and in contrast, Mn^+ from dissociation of the corresponding manganese complexes. Similar observations have been made following CID studies of single metal complex ions $ML_n{}^+$ (M = Zn or Mn; L = Pr or Fr; n = 1–5, not shown here). These observations can be explained by differences in the ionization energies of the constituents, the values of which are summarized in Table 1 [32]. Because the IE's of pyrrole and furan are both lower than that of Zn, CID favours appearance of the pyrrole and furan cations. In contrast, Mn^+ appears following the CID of Mn_2L^+ (L = Pr or Fr), because the IE of manganese is lower than that of either pyrrole or furan.

Pyrrole and furan are aromatic five-membered rings and are both capable of acting as six-electron donors. In contrast to benzene, they also have lone pair electrons that are available for donation to the metal ion: one pair on the nitrogen atom of pyrrole and two lone pairs on the oxygen atom of furan. Hence, there are two possible forms of bonding to metal atoms: N-end for pyrrole and O-end for furan lone-paired σ-orbital bonding and π-orbital bonding. Although five-membered heterocyclic ligands are poorer electron donors than benzene and pyridine, many examples can be found in the literature of such complexes in the condensed phase [33], and gas phase studies [34]. Previous studies carried out in condensed phases have shown that pyrrole can N-bond to metal centers [35–38]. However, density functional calculations carried out by Dunbar [7] indicate that pyrrole is somewhat unique among nitrogen heterocycles in that π-site bonding is preferred over N-site bonding in both singly-ligated M^+(pyrrole) and doubly ligated $M^+(\mathrm{pyrrole})_2$ cations. Binding at the nitrogen atom in pyrrole is inhibited by the accumulation of positive charge that results in strong electrostatic repulsion with the metal cation, therefore, no favourable binding sites could be identified for any metal cation in the vicinity of nitrogen. To date, there have been very few corresponding experimental or theoretical studies of the geometric structures of related molecules with transition metal clusters of the form M_mL_n with $m > 1$ and $n > 1$ [14].

The evidence obtained from these CID results is not enough to give unequivocal information about the structures of the ions. However, sandwich structures, containing a pyrrole or furan molecule between the two metal atoms seem unlikely. Sandwich structures, for example, are unlikely to lead to either $Mn_2{}^+$ or $Zn_2{}^+$ as fragments. It is most probable that the two atoms bond with each other with only one metal atom directly bonded to the ligand.

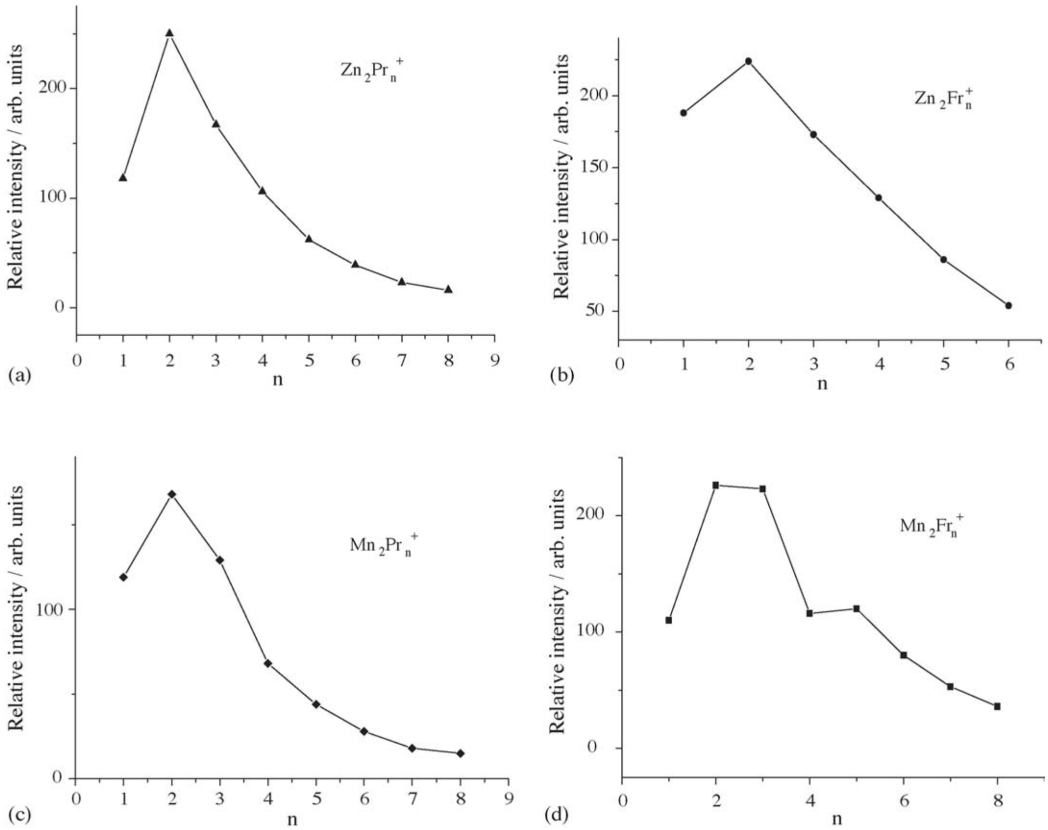

Fig. 2. Relative intensities of complexes plotted as a function of n: (a) $Zn_2(\mathrm{pyrrole})_n{}^+$, (b) $Zn_2(\mathrm{furan})_n{}^+$, (c) $Mn_2(\mathrm{pyrrole})_n{}^+$ and (d) $Mn_2(\mathrm{furan})_n{}^+$.

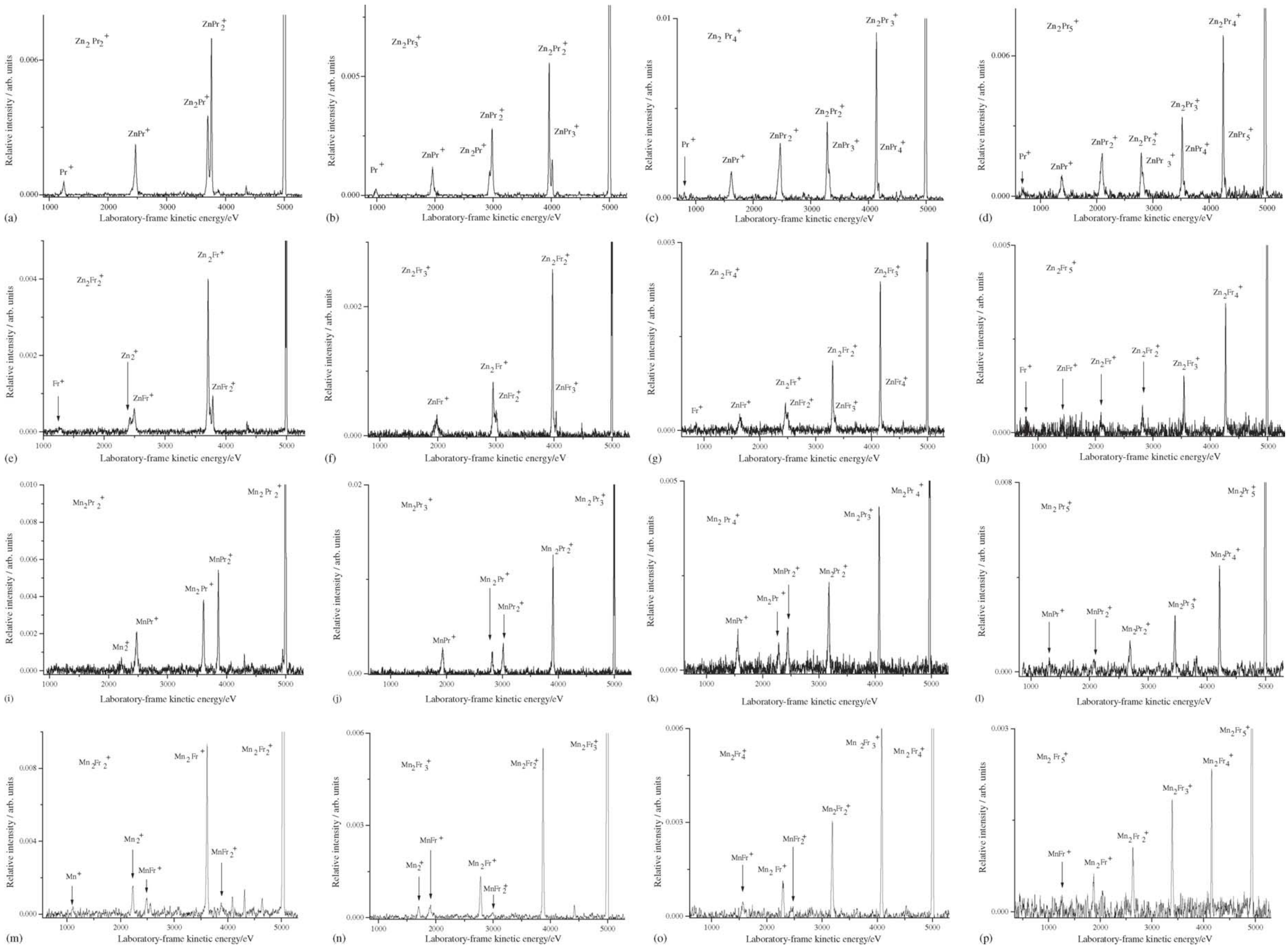

Fig. 3. Ion kinetic energy (MIKE) spectra recorded following the collisional activation of (a–d) $Zn_2Pr_n^+$, (e–h) $Zn_2Fr_n^+$, (i–l) $Mn_2Pr_n^+$ and (m–p) $Mn_2Fr_n^+$.

3.2. $M_2L_n^+$ ($n = 2$–5) complexes and their collision-induced fragmentation patterns

Up to eight molecules of pyrrole and furan have been observed to attach to the two metal cations to form stable gas phase complexes $M_2L_n^+$. Fig. 2 shows the relative intensities of the $M_2L_n^+$ ions for up to $n = 8$, where it can be seen from Fig. 2a and c that, as far as pyrrole is concerned, the most intense ions contain two ligand molecules. The existence of a maximum in an intensity distribution could be linked to the presence of a stable structure. In contrast to pyrrole complexes, the most intense ions for furan complex ions, in the corresponding series complex, are 1 and 2 for $Zn_2Fr_n^+$ and 2 and 3 for $Mn_2Fr_n^+$, respectively. Although there appear to be no ions with intensities significant different from those of their immediate neighbors, the fact that all four systems do peak at $n = 2$, does suggest the formation of stable structures.

Fig. 3 show the results of experiments undertaken on the collision-induced fragmentation of size-selected complex ions $M_2L_n^+$ ($n = 2$–5), and summarized in Table 2 are the observed fragmentation products. Several interesting trends are immediately observed. The primary fragmentation routes are the loss of either a neutral metal atom or a ligand molecule from the corresponding parent ion, and since ionization/collisional activation can deposit a broad distribution of energy into an ion, a competition between these two pathways is likely. All furan complex ions show a strong preference for the loss of furan (M_2L^+ results have been discussed above), and slightly less favorable, is the loss of a metal atom on the part of pyrrole complexes with small number of ligands ($n = 1, 2$). These results confirm an earlier conclusion, which is that furan appears to be less strongly bound to either Zn_2^+ or Mn_2^+. Also evident from Table 2 and Fig. 3 is that, in the case of manganese, complexes containing more than two ligand molecules do not lose isolated neutral metal atoms from the parent ion directly, but metal atom loss is seen only when accompanied by one or more ligand molecules. Since the experiment only provides information on the total mass of the neutral loss, it is not possible to determine if the metal atoms and molecules are lost as separate entities. In contrast to manganese, the loss of a zinc atom from $Zn_2L_n^+$ complexes is observed up to $n = 4$ for $Zn_2(\text{furan})_n^+$, and up to $n = 5$ for $Zn_2(\text{pyrrole})_n^+$. In several instances, particularly at larger n, the appropriate peak is only distinguishable as a shoulder on a more intense fragment ion. In part, this difference between manganese and zinc may be related to bond energy, but a more likely source is ionization energy. Formation of the zinc dimer does not lead to a substantial drop in IE, with the result that both pyrrole and furan still have IE's that are lower than that of Zn_2. Thus, the positive charge may well reside on the molecular component of a complex, which means that the weak bond of neutral Zn_2 is easily broken. Again, such behaviour is also related to the appearance of the molecular ions Fr^+ and Pr^+ following the CID of smaller zinc dimer complexes.

For comparison purposes, the ratio of the loss of a ligand molecule to loss of a metal atom from the same parent complex ions, M_2L^+-M/M_2L^+-L, has been calculated and the values listed in Table 3. For each series of complexes, the ratio of M_2L^+-M/M_2L^+-L decreases as n increases, up to the point where loss of a metal atom cannot been seen from any of the larger complexes. This is not unexpected considering that in general the

Table 2
Fragment ions formed following the collisional activation of $Zn_2(\text{pyrrole})_n^+$, $Zn_2(\text{furan})_n^+$, $Mn_2(\text{pyrrole})_n^+$ and $Mn_2(\text{furan})_n^+$, all for $n = 1$–5

Starting complex	Ionic fragments				
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
$Zn_2Pr_n^+$	$ZnPr^+$, Zn_2^+ Pr^+	$ZnPr_2^+$, Zn_2Pr^+ $ZnPr^+$ Pr^+	$ZnPr_3^+$, $Zn_2Pr_2^+$ $ZnPr_2^+$, Zn_2Pr^+ $ZnPr^+$ Pr^+	$ZnPr_4^+$, $Zn_2Pr_3^+$ $ZnPr_3^+$, $Zn_2Pr_2^+$ $ZnPr_2^+$, Zn_2Pr^+ $ZnPr^+$ Pr^+	$ZnPr_5^+$, $Zn_2Pr_4^+$ $ZnPr_4^+$, $Zn_2Pr_3^+$ $ZnPr_3^+$, $Zn_2Pr_2^+$ $ZnPr_2^+$ $ZnPr^+$ Pr^+
$Zn_2Fr_n^+$	$ZnFr^+$, Zn_2^+ Fr^+	$ZnFr_2^+$, Zn_2Fr^+ $ZnFr^+$, Zn_2^+ Fr^+	$ZnFr_3^+$, $Zn_2Fr_2^+$ $ZnFr_2^+$, Zn_2Fr^+ $ZnFr^+$	$Zn_2Fr_3^+$ $ZnFr_3^+$, $Zn_2Fr_2^+$ $ZnFr_2^+$, Zn_2Fr^+ $ZnFr^+$ Fr^+	$Zn_2Fr_4^+$ $Zn_2Fr_3^+$ $Zn_2Fr_2^+$ Zn_2Fr^+ $ZnFr^+$ Fr^+
$Mn_2Pr_n^+$	$MnPr^+$, Mn_2^+ Mn^+	$MnPr_2^+$, Mn_2Pr^+ $MnPr^+$, Mn_2^+	$Mn_2Pr_2^+$ $MnPr_2^+$, Mn_2Pr^+ $MnPr^+$	$Mn_2Pr_3^+$ $Mn_2Pr_2^+$ $MnPr_2^+$, Mn_2Pr^+ $MnPr^+$	$Mn_2Pr_4^+$ $Mn_2Pr_3^+$ $Mn_2Pr_2^+$ $MnPr_2^+$ $MnPr^+$
$Mn_2Fr_n^+$	$MnFr^+$, Mn_2^+ Mn^+	$MnFr_2^+$, Mn_2Fr^+ $MnFr^+$, Mn_2^+ Mn^+	$Mn_2Fr_2^+$ $MnFr_2^+$, Mn_2Fr^+ $MnFr^+$, Mn_2^+	$Mn_2Fr_3^+$ $Mn_2Fr_2^+$ $MnFr_2^+$, Mn_2Fr^+ $MnFr^+$	$Mn_2Fr_4^+$ $Mn_2Fr_3^+$ $Mn_2Fr_2^+$ Mn_2Fr^+ $MnFr^+$

Table 3
Intensity ratios $M_2(L)_n^+$-M/$M_2(L)_n^+$-L

Complex	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
$Zn_2Pr_n^+$	3.6	1.0	0.3	0.1	0.1
$Zn_2Fr_n^+$	0.9	0.2	0.1		
$Mn_2Pr_n^+$	3.5	1.4			
$Mn_2Fr_n^+$	0.41	0.1			

binding energies of ligands should decrease as the total number of ligands increases. In addition, the ligands might also be expected to envelope both metal atoms rather than bind to just one.

It is worth noting that among the four $M_2L_2^+$ complexes, the ratio of $M_2Pr_2^+$-M/$M_2Pr_2^+$-Pr is the largest, and the ratio of $M_2Fr_2^+$-M/$M_2Fr_2^+$-Fr is the smallest. From this observation, we would suggest that it is relatively hard to lose a pyrrole molecule and relatively easier to lose a furan molecule. It is also interesting to note that for both sets of $M_2Pr_n^+$, there is an abrupt decline in the M_2L^+-M/M_2L^+-L intensity after $n = 2$, which could indicate a significant change in geometry.

From these observations it would appear reasonable to assume that both metal atoms bind to each other and that there is no evidence to suggest the formation of sandwich structures. When n is greater than 2, the two metal atoms remain bound together, and for manganese the ligands bind to a metal ion core. For zinc complexes, there is the possibility they adopt a staircase structure, as suggested by Majumdar et al. [14] for a cluster of benzene with platinum (Bz_3–Pt_2). In pyrrole complexes, $M_2Pr_n^+$ at high n, pyrrole molecules have a possibility to bond to each other by self-association through N–H···Π hydrogen bonding [39]. For furan complexes $M_2Fr_n^+$ at high n, it is possible that a O···H–C hydrogen bond might form between furan molecules. Such interactions would be enhanced by the presence of a cooperation involving more than one hydrogen bond.

4. Conclusion

It has been shown that the pick-up technique can be used successfully to prepare complexes containing metal dimers. In the two examples presented here, their fragmentation patterns have revealed details of a qualitative picture of the arrangements of molecules surrounding the metal core. In particular, the metal dimers appear to remain intact following the formation and ionization of the complexes.

Acknowledgement

The authors would like to thank EPSRC for financial support for this project.

References

[1] D.H. Russell (Ed.), Gas Phase Inorganic Chemistry, Plenum Press, New York, 1989.
[2] P.B. Armentrout, Ann. Rev. Phys. Chem. 41 (1990) 313;
K. Eller, H. Schwarz, Chem. Rev. 91 (1991) 1121.
[3] D.A. Dougherty, Science 271 (1996) 163.
[4] R. Bakhtiar, D.B. Jacobson, J. Am. Soc. Mass Spectrom. 7 (1996) 938.
[5] V.K. Nanayakkara, B.S. Freiser, J. Mass Spectrom. 32 (1997) 475.
[6] D. Stöckigt, J. Phys. Chem. A 101 (1997) 3800.
[7] A. Gapeev, C.-N. Yang, S.-J. Klippenstein, R.C. Dunbar, J. Phys. Chem. A 104 (2000) 3246.
[8] R.T. Grimm, J.B. Mangrum, R.C. Dunbar, J. Phys. Chem. A 108 (2004) 10897.
[9] P.H. Su, C.S. Yeh, Chem. Phys. Lett. 331 (2000) 420.
[10] M.J. Schadt, A.J. Lees, Inorg. Chem. 25 (1986) 672;
S. Zhan, G.R. Dobson, Inorg. Chem. 29 (1990) 598.
[11] D.C. Parent, S.L. Anderson, Chem. Rev. 92 (1992) 1541.
[12] A. Kaldor, D.M. Cox, M.R. Zakin, Adv. Chem. Phys. 70 (1988) 211.
[13] C.T. Rattner, M.N. Ashfold (Eds.), Dynamics of Gas-Surface Interactions, The Royal Society of Chemistry, Cambridge, 1991.
[14] D. Majumdar, S. Roszak, K. Balasubramanian, J. Chem. Phys. 114 (2001) 10300.
[15] V.K. Nanayakkara, B.S. Freiser, J. Mass Spectrom. 32 (1997) 475.
[16] P.-H. Su, F.-W. Lin, C.-S. Yeh, J. Phys. Chem. 105 (2001) 9643.
[17] K. Ervin, S.K. Loh, N. Aristov, P.B. Armentrout, J. Phys. Chem. 87 (1983) 3593.
[18] M.F. Jarrold, A.J. Illies, M.T. Bowers, J. Am. Chem. Soc. 107 (1985) 7339.
[19] R. Houriet, T. Vulpius, Chem. Phys. Lett. 154 (1989) 454.
[20] A. Terasaki, A. Matsushita, K. Tono, R.T. Yadav, T.M. Briere, T. Kondow, J. Chem. Phys. 114 (2001) 9367.
[21] G.L. Gutsev, C.W. Bauschlicher Jr., J. Phys. Chem. A 107 (2003) 4755.
[22] G.L. Gutsev, M.D. Mochena, P. Jena, C.W. Bauschlicher Jr., H. Partridge III, J. Chem. Phys. 121 (2004) 6785.
[23] B.S. Larsen, R.B. Freas III, D.P. Ridge, J. Phys. Chem. 88 (1984) 6014.
[24] K.D. Carlson, K.R. Kuschnir, J. Phys. Chem. 68 (1964) 1566.
[25] S.W. Buckner, J.R. Gord, B.S. Freiser, J. Chem. Phys. 88 (1988) 3467.
[26] M.T. Rodgers, J.R. Stanley, R. Amunugama, J. Am. Chem. Soc. 122 (2000) 10969.
[27] R. Amunugama, M.T. Rodgers, J. Phys. Chem. A 105 (2001) 9883.
[28] M.T. Rodgers, P.B. Armentrout, J. Am. Chem. Soc. 124 (2002) 2678.
[29] I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, Science 305 (2004) 1136.
[30] N.R. Walker, R. Wright, A.J. Stace, J. Am. Chem. Soc. 121 (1999) 4837.
[31] M.T. Rodgers, J.R. Stanley, R. Amunugama, J. Am. Chem. Soc. 122 (2000) 10969.
[32] NIST Chemistry Web Book, NIST Standard Reference Database (http://webbook.nist.gov/chemistry/).
[33] P. George, Chem. Rev. 75 (1975) 85.
[34] R. Bakhtiar, D.B. Jacobson, J. Am. Soc. Mass Spectrom. 7 (1996) 938.
[35] K.M.K. Dailey, T.B. Rauchfuss, A.L. Rheingold, G.P.A. Yap, J. Am. Chem. Soc. 117 (1995) 6396.
[36] L.M. Hodges, J. Gonzalez, J.I. Koontz, W.H. Myers, W.D. Harman, J. Org. Chem. 58 (1993) 4788.
[37] R. Cordone, W.D. Harman, H. Taube, J. Am. Chem. Soc. 111 (1989) 5969.
[38] B. Chaudret, F.A. Jalon, J. Chem. Soc. Chem. Commun. (1988) 711.
[39] V. Stefov, L. Pejov, B. Šoptrajanov, J. Mol. Struct. 649 (2003) 231.