DALTON
FULL PAPER

Aqueous co-ordination chemistry using electrospray mass spectrometry of anions: metal(VI)–monosaccharide complexes (M = W or Mo)

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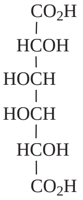
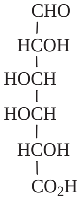
Electrospray mass spectrometry has been applied for the first time to the co-ordination chemistry of aqueous anions, using as a model system the reaction of tungstate or molybdate with galactaric (mucic) acid and galacturonic acid; 1 : 1, 2 : 1 and 1 : 2 complexes are found, thus confirming and extending previous solution-state studies. The gas-phase ions may undergo minor dehydration, and some decarboxylation. Nevertheless, the method is shown to provide a rapid and simple means for identifying mixtures of anionic complexes in dilute aqueous solution, even when their binding constants are modest.

Electrospray ionisation mass spectrometry (ESI-MS) is a very gentle, rapid and essentially non-selective technique for transferring existing ions from dilute solutions into the gas phase and identifying them. It therefore has considerable potential for the investigation of complex inorganic systems in dilute solution. In a recent paper we have discussed earlier MS experiments in other media, and have shown that ESI-MS can also be applied to purely aqueous solutions of anions, specifically polyoxo-tungstates and -molybdates.[1] As well as the known species, *e.g.* $[WO_4]^{2-}$, $[H_2W_{10}O_{32}]^{2-}$ and $[H_8W_{12}O_{42}]^{4-}$, several other anions were extracted for the first time from aqueous solution, including $[HW_2O_7]^-$ and $[W_6O_{19}]^{2-}$. Although minor chemical changes may result from the transfer to the gas phase, such as the reduction of charge by protonation or metallation, the method nevertheless gives a practical, semiquantitative guide to the detailed composition of the species present. It can also track kinetic processes on a timescale of minutes.

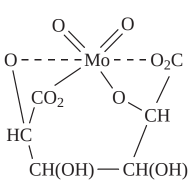
It is timely to find out whether the same method can be applied more generally, to investigate co-ordination by ligands other than oxo or hydroxo. Do these ligands remain bound in the gas phase, under conditions that remove outer-sphere water? Are the spectra readily interpretable, or are they unduly complicated by *e.g.* clustering or by decomposition products? Our strategy has been to study an aqueous system that is already largely understood from NMR studies, under conditions where the ligand binding is known to be not particularly strong, and the ligands themselves vulnerable to dehydration or decarboxylation. The open-chain structures of the chosen ligands, galactaric (mucic) acid, abbreviated here to gta, and galacturonic acid, here gtu, are given below. Galacturonic acid was normally observed in its dehydrated, aldehyde or pyranose form in the gas phase, and this is implicit in the formulae given below. Both acids are known to interact with tungstate, $[WO_4]^{2-}$, and with molybdate, $[MoO_4]^{2-}$, to give complexes with metal : ligand ratios 1 : 1 and 2 : 1.[2,3] Two of the structures proposed from the NMR data are illustrated below, although their protonation state is not specified. They correspond to the anions labelled **d** and **h** in the present paper. The 1 : 1 species are also reported to be in equilibrium with 2 : 2 species at concentrations around 1 mol dm^{-3}, but such oligomers are unlikely to be significant at the millimolar concentrations appropriate to ESI-MS, unless they form in the final stages of evaporation of the solution droplets, and then resist dissociation in the gas phase. 2 : 2 Species are not in fact observed in the present study. The binding constants are not explicitly quoted in the earlier work, but the data presented for galactaric acid plus either tungstate or molybdate imply that these should be somewhat less than 50% complexed, under the conditions used below. Species with a 1 : 2 ratio are also reported with a related ligand.[4] Similar complexes between carbohydrates and transition-metal ions are important in many biological processes.[5] For example, extracellular polysaccharides that are produced by many bacteria in plant species are thought to bind molybdenum through uronic acid residues.[6,7] As a consequence, the Mo available to the plant as a micronutrient is reduced.

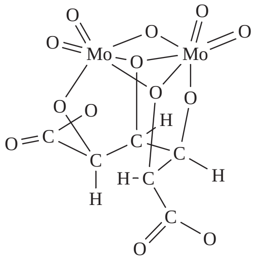


gta



gtu





The ESI-MS results should be complementary in many ways to the earlier work. They will yield little structural information. However, there should be no complications from rapid exchange processes, or from any paramagnetic species that might be present, and the masses *m* and charges *z* of each ion should be unambiguously determinable. Although mass spectroscopy only measures *m*/*z* directly, nevertheless *z* is readily

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determined either from the characteristic isotope structures of the peaks (^{182}W, ^{183}W, ^{184}W and ^{186}W; ^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo and ^{100}Mo) or from the change in *m*/*z* upon replacement of H by either Li or Na. In fact, only $z = 1$ complexes are detected here, although $z = 2$ or 3 polyoxoanions are also seen, as previously, in species where no saccharide ligand is present.[1] The ESI-MS technique also has the potential for studies at biologically and environmentally realistic concentrations.

In order to make the spectra comparable, all measurements were carried out using 5×10^{-3} mol dm^{-3} solutions at pH values between 5.6 and 6.0. It is not possible to be precise about the concentrations, temperature or pH at the moment of entry into the gas phase, because this entry is achieved by the rapid evaporation of tiny droplets, charged electrolytically, and heated in the present case to 80 °C just before evaporation. The pH 5–6 region is also interesting in polyoxo-tungstate and -molybdate chemistry alone, for the monomeric anions start to form oligomers below pH *ca.* 7, so that several different species should coexist under the present conditions.

For the above reason of comparability, most measurements were carried out at a 1 : 1 ratio of metal to ligand, as this is reported to maximise the proportions of bound species.[2,3] However, a preliminary study at other ratios demonstrated only the expected extra contributions to peak intensity from either free monoanionic carbohydrate or free metalate ions. The variations in peak heights were in semiquantitative agreement with the stoichiometric predictions, and no new peaks appeared. One advantage of the chosen system is that the binding is essentially between anions, so that free metal and free carbohydrate are detected in the same spectrum as the complexes.

Experimental

All experiments were performed by means of a Quattro II Q*h*Q tandem quadrupole instrument (Micromass, Manchester) fitted with an electrospray ionisation source operated in negative ion mode. The tip of the capillary and the sampling cone were maintained at potentials of +3 kV and +35 V respectively, relative to ground. Separate experiments showed that the spectra were rather insensitive to this cone voltage in the range 25–100 V, although further fragmentation is detectable above 75 V. The source temperature was 80 °C. The mobile phase consisted of water with no additives and the optimum flow rate of the mobile phase was found to be 10 μl min^{-1}. A Rheodyne injector fitted with a 20 μl loop was used to inject the sample solution into the mobile phase.

Mass spectra were acquired by scanning the first quadrupole mass analyser from *m*/*z* 2000 to 100 and ions were detected by means of a scintillator detector positioned after the first quadrupole. Collision induced dissociation (CID) spectra were obtained by selecting a given complex ion in the first quadrupole and passing it into the collision cell containing argon gas. The pressure and the voltages applied to the collision cell were set to 1.5×10^{-3} mbar (0.15 Pa) and 25 V respectively. The second quadrupole mass analyser was scanned to give a spectrum of the product ions produced. Approximately 25 scans were summed to give mass spectra and fragment ion spectra. All data were processed by means of the MassLynx data system (Micromass).

Galactaric and galacturonic acids, lithium and sodium tungstate and lithium and sodium molybdate were from Sigma-Aldrich Chemical Company, May and Baker Ltd. and Fisons respectively. All chemicals were used without further purification. Mixed aqueous solutions were made to concentrations of 5×10^{-3} mol dm^{-3} and a metal to carbohydrate ratio of 1 : 1, unless stated otherwise. The pH values of these solutions, measured by means of a standard pH meter (Hanna Instruments, Bedfordshire), ranged from 5.6 to 6.0.

Results and Discussion

The spectra to be described below have many types of anions in common, although the masses vary between spectra as the metal, ligand and counter ion is varied. These types are readily identified in most cases, as described above. In some cases their identification was confirmed by other spectra run under closely similar conditions. In all the figures below they are labelled as follows.

Metal-free species

The uncharged carbohydrates gta and gtu are polybasic towards tungstate and molybdate, and may conveniently be generalised as H_5A. Their Fischer projection formulae are given above. Their monoanions $[H_4A]^-$ are all labelled **a**. No dianions were clearly detected, although such detection would in fact be problematic because the *m*/*z* region below 150 in ESI-MS spectra is normally complicated by peaks from *e.g.* small, charged solvent clusters and related fragments. The spectra involving gtu also show acid dimer peaks, marked **l**, with formulae $[H_9A_2]^-$, presumably because of weaker binding to metal and hence higher concentrations of free acid and its anion. Indeed, a spectrum of gtu alone shows a series of peaks corresponding to $[H_4A(H_5A)_n]^-$, with decreasing heights as *n* increases from 1 to 4. Metallated species are also observed. Singly lithiated anions are denoted in all cases by a single prime, so that *e.g.* $[LiH_8A_2]^-$ becomes **l′**, and the corresponding sodiated species are identified by a double prime, *e.g.* **l″** for $[NaH_8A_2]^-$. However, acid clusters with $n > 1$ are not seen in any spectra where W or Mo is present. Also, species with more than one bound alkali metal are not detected in any spectrum, and there is no evidence for decarboxylation of either acid, in the absence of W or Mo.

Metal–saccharide complexes

Again, only $z = 1$ anions are found. The simplest, 1 : 1 species, $[MO(A)]^-$, labelled **c**, are not found in metallated forms because they have no readily exchangeable hydrogens. Since A has a formal 5− charge, and because alkoxide moieties are unlikely to exist unbound, the formula $[MO(A)]^-$ probably implies five- or six-co-ordinate M. Decarboxylated species $\mathbf{c}^\circ = \mathbf{c} - CO_2$ and $\mathbf{c}^{\circ\circ} = \mathbf{c} - 2CO_2$ are also detected at lower abundances, especially when M = Mo. This decarboxylation process is discussed further below. The hydrated species $[H_2MO_2A]^-$ **d** and $[H_4MO_3A]^-$ **e** are also found in some cases. These are found in mono-lithiated and -sodiated forms, **d′**, **d″**, *etc.* Thus **e′** is the species $[LiH_3MO_3A]^-$.

A second series consisting of 2 : 1 complexes is also found. Species **g** are $[M_2O_4A]^-$, and the hydrated forms **h**, $[H_2M_2O_5A]^-$, are also metallated as **h′** and **h″** in some spectra. The earlier NMR study strongly suggested that these anions are built round an M_2O_5 core.[2,3] Anions **g** and **h** are also sometimes found in the decarboxylated forms $\mathbf{g}^\circ = \mathbf{g} - CO_2$, *etc.*

A third, more hydrated series of 1 : 2 complexes is also detected: **j**, $[H_5MOA_2]^-$; **k**, $[H_7MO_2A_2]^-$, and their metallated forms. Possible parent ions, **i**, $[H_3MA_2]^-$, may also be just detectable.

Metal-only species

All spectra show a strong signal **b** from $[HMO_4]^-$. Although metallated forms of **b** are known from earlier work, they are not significant here.[1] Other previously reported peaks are **f**, $[HM_2O_7]^-$, and **q**, $[W_6O_{19}]^{2-}$, with *m*/*z* 704. Four other previously unidentified isopolytungstates may also be tentatively identified as peaks **o**, $[W_4O_{13}]^{2-}$ (at *m*/*z* 472), **p′**, $[LiW_3O_{10}]^-$ (*m*/*z* 719), **r**, $[HW_{10}O_{32}]^{3-}$ (*m*/*z* 784.3), possibly overlapping **r′** at *m*/*z* 786.3 also, and **s′**, $[LiH_6W_{12}O_{41}]^{3-}$ (*m*/*z* 959) or **s″**, $[NaH_6W_{12}O_{41}]^{3-}$ (*m*/*z* 964.3), either of these possibly also overlapping **s** at *m*/*z* 957. Although dinegative species similar to **o**, **p**,

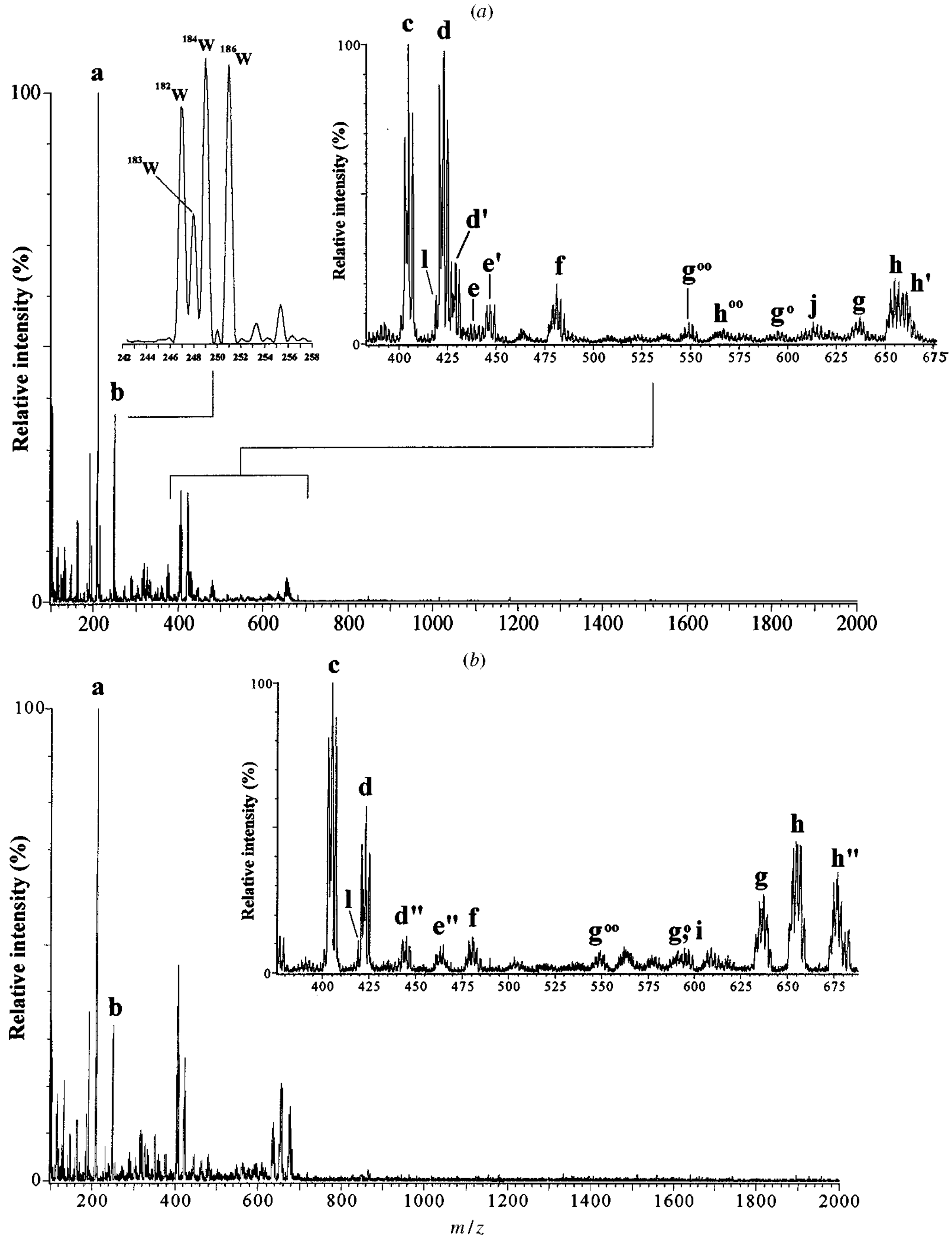

Fig. 1 The ESI mass spectra of an aqueous solution, 2.5 mmol dm^{-3} in both tungstate and galactarate, pH 6.0. The main inset is an expansion, and the small inset a further expansion to show the characteristic isotope pattern for a species with a single W. Counter ions: (*a*) Li$^+$, (*b*) Na$^+$. Peak labels as in text and Table 1

r and **s** were reported previously, the trinegative species may have been present here because of a fortunate choice of pH. The spectra presented below confirm that metallation is not possible for species **o** or **p**$^{2-}$ (*i.e.* the dinegative form, *m*/*z* 357) in accordance with their lack of exchangeable hydrogens.

The spectra are now discussed in detail. Fig. 1(*a*) and 1(*b*) show the species derived from tungstate + gta, with Li$^+$ or Na$^+$ respectively as counter ions. Some areas are expanded to show the isotopic distributions more clearly. As expected, the dominant complexes are of types **c** and **d**, with **d**″ more clearly separated from **d** than is **d**′. This shows the analytical value of varying the counter ion. The more hydrated form, **e**, occurs preferentially in its metallated forms **e**′ and **e**″, perhaps for the same reason as suggested above for the acid dimers. Similar observations apply to the W$_2$A species **g**, **h**, **h**′ and **h**″. Weak WA$_2$ signals from **i** and **j** may also be just detectable. Other, minor signals probably arise *via* loss of CO$_2$ from *e.g.* **g** and **h**, or from other minor breakdown products. The total extent of complexation may be estimated from the relative intensities of the various signals. It is similar to that deduced from the earlier NMR data. Hence the ESI process does not markedly dissociate the complexes known to be present in the original solution.

The proposed decarboxylation is demonstrated by a parallel experiment on the same (Li$^+$) sample. The ions of mass 423, *i.e.* from the ^{184}W isotope of **d**, were selected and then subjected to collision-induced dissociation as described above. The resulting species must derive solely from this parent ion. They correspond, in decreasing order of mass, to **c**, **c**°, **c**°° and **b**, as shown in Fig. 2. The double decarboxylation is more prominent under these more violent conditions. The extent of decarboxylation thus demonstrated is probably sufficient to explain the corresponding peaks in Fig. 1(*a*) and 1(*b*).

It is also evident from Fig. 2 that the **c** peaks in the other

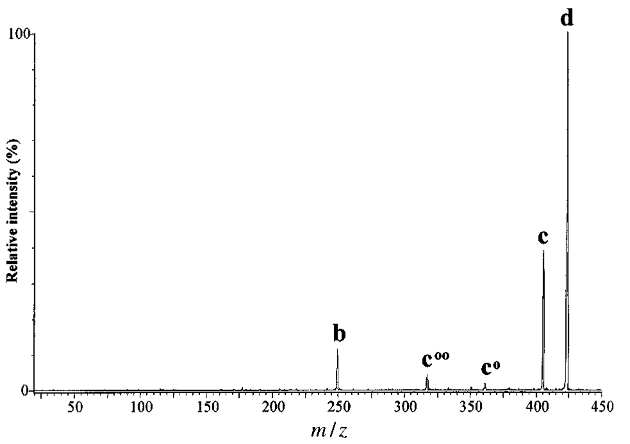

Fig. 2 The CID spectrum from the same sample as in Fig. 1(*a*). The ^{184}W isotopomer of species **d** was selected for collision with Ar. The peaks at lower mass are its decomposition products. Peak labels as in text and Table 1

spectra may contain a component from the gas-phase decomposition of **d**. Does **c** actually exist in solution, or is it solely the product of the ESI process? The small relative size of the **c** peak in Fig. 2 shows that the CID process alone is insufficient to explain the substantial magnitude of the **c** signal in Fig. 1(*a*) and 1(*b*). It follows either that **c** is indeed present in the original solution, or else that substantial dehydration of **d** also takes place during the initial process of droplet evaporation, prior to any collisions. The NMR evidence is only for one set of signals in solution, but these could arise from a rapid hydration equilibrium between **c** and **d**. Therefore the original question must remain open, pending more detailed experiments.

Fig. 1(*a*) and 1(*b*) contain no evidence for complexes with $z = 2$ or higher. Thus the 2:2 ion $[H_2W_2O_4A_2]^{4-}$, proposed by Gil *et al.*, is not seen at *m*/*z* 211, and neither is its protonated $z = 2$ form at *m*/*z* 423, for this would have a quite different isotopic pattern from the signal for **d** that is actually observed. A single negative charge is in fact quite normal for similar dissolved anions in this pH range.

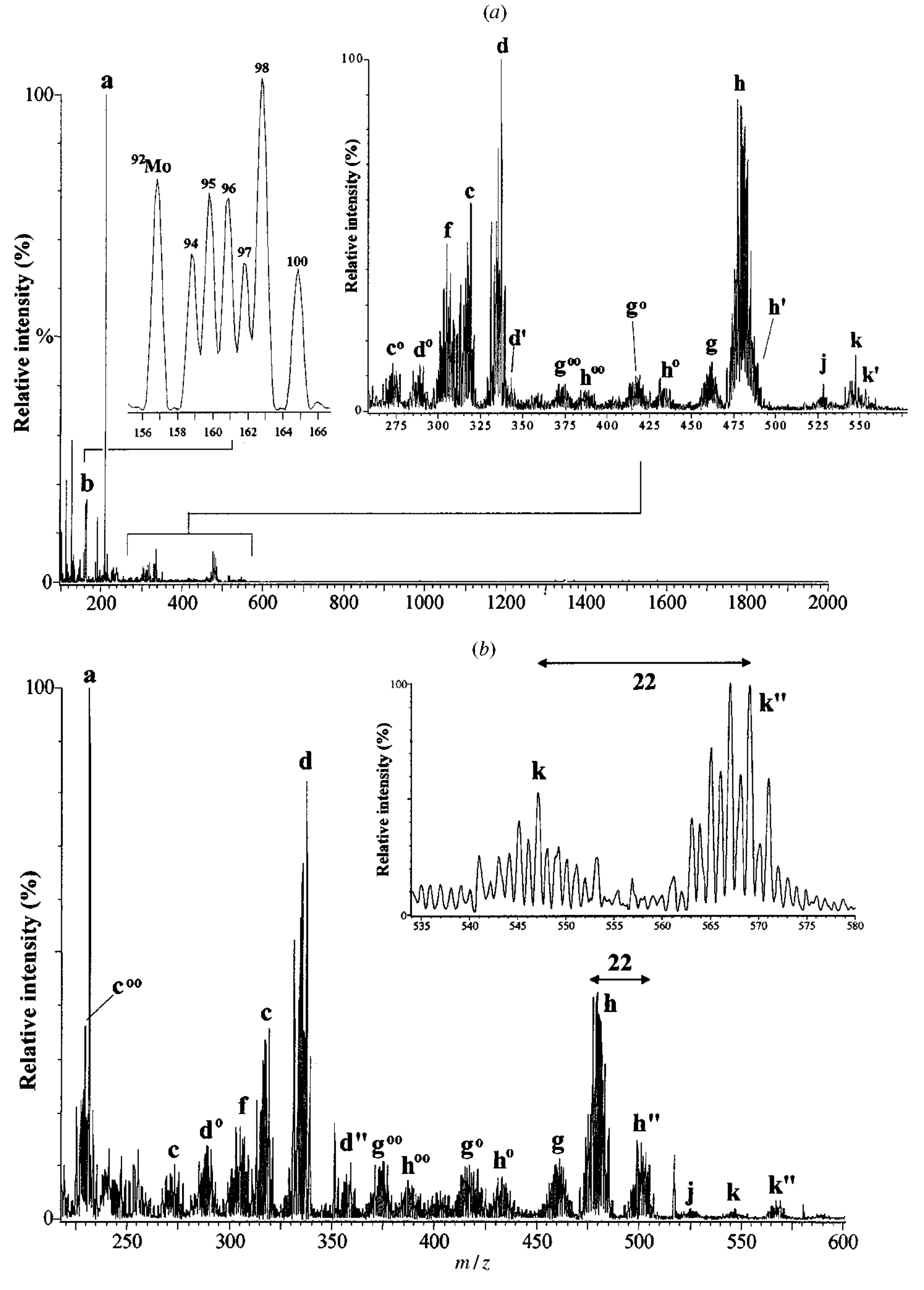

Fig. 3 Spectra as in Fig. 1, except that Mo replaces W throughout

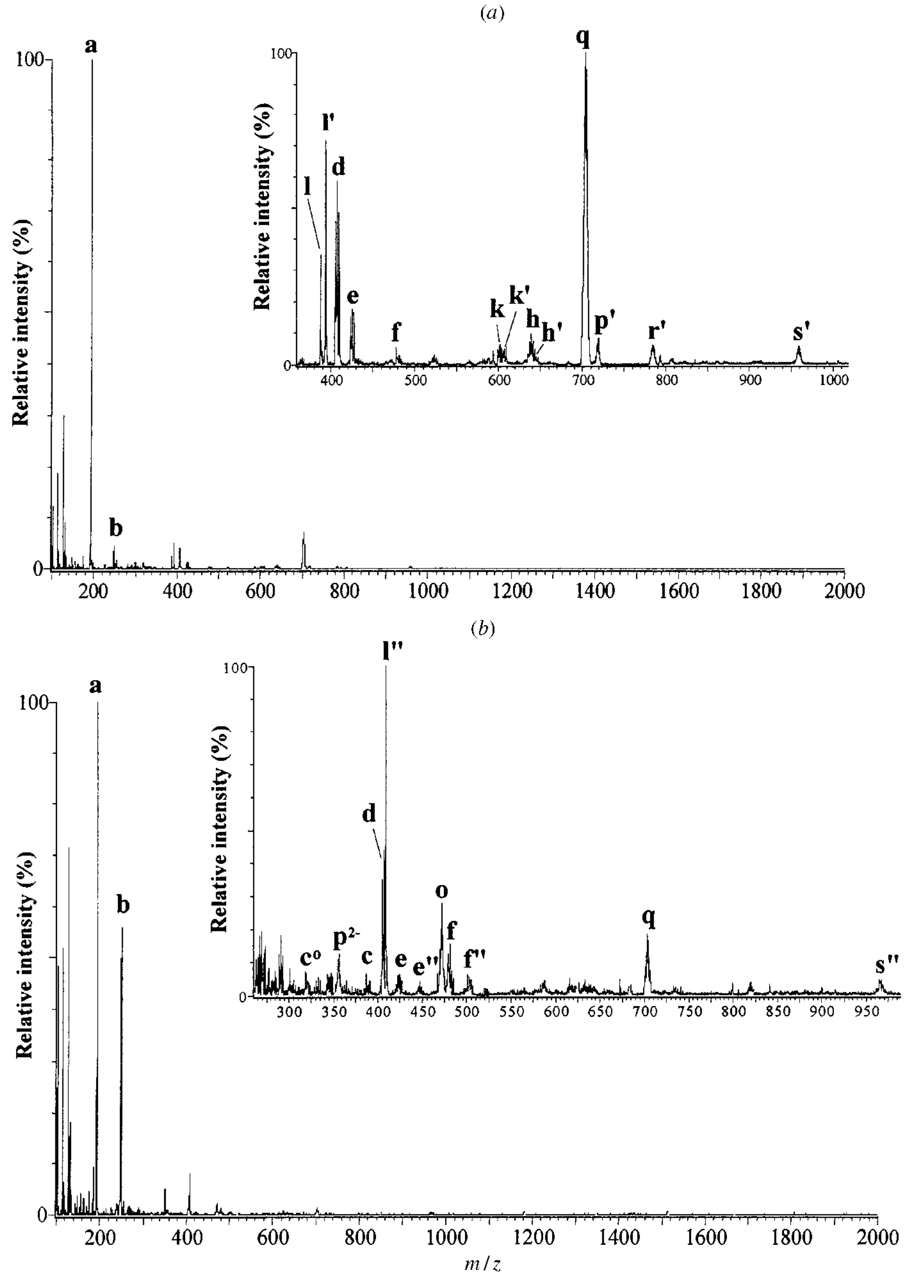

Fig. 4 Spectra as in Fig. 1, except that galacturonate replaces galactarate throughout

Fig. 3(*a*) and 3(*b*) show the corresponding spectra when Mo has replaced W. The isotope pattern for Mo is more complex, so that only the peak clusters from the sodiated species now lie clear of the protonated ones. The species are similar to those with W, but are now more likely to be hydrated. Thus **j**, **k**, **k**′ and **k**″ are now detected, but not **i**. An expansion of the **k** and **k**′peaks is shown in Fig. 3(*b*), to indicate the actual resolution achieved. Similarly, **d** is now larger than **c**, and **h** much larger than **g**. Decarboxylated and doubly decarboxylated forms of **c**, **d**, **g** and **h** are also seen, though not dominant. The greater tendency to hydration of the molybdenum species may relate to the generally lower formation constants for Mo, relative to W.[8] One potential alkoxy ligand may remain instead as an unco-ordinated OH group, replaced on Mo by $[OH]^-$. The presence of decarboxylated complexes is consistent with the proposal by Gil *et al.* that the carboxylate group is not necessarily involved in the co-ordination of the MA or the MA_2 species.

Fig. 4(*a*) and 4(*b*) are a little different, although many cognate species are present. Galacturonic acid is likely to bind more weakly than galactaric acid, because it exists mainly in a furanose ring form, and is proposed to bind to the metal in this form.[9] Hence the spectra show less complexation and more free galacturonate, plus balancing tungstates and isopolytungstates appropriate to the pH. Most of the previous types of complex are nevertheless observed, notably **c**, **d**, **e**, **g** and **h**, with **d** being the strongest. However, the WA_2 species **i** and **j** are replaced by the hydrated forms **k** and **k**′, in Fig. 4(*a*). This may reflect hydration at the aldehyde moiety of the galacturonate. Also, metallated species are less apparent here, perhaps because of the missing carboxylate group.

The other peaks in these two spectra reflect the higher concentrations of both the acid and of tungstate. The component monomers **a** and **b** are now very marked. Also the sodiated acid dimer **l**″ appears, along with the tungstate oligomers **f**, **o**, $\mathbf{p}^{2-}$, **q** and **s**, **s**′, **s**″, as listed at the beginning of this section. The relative proportions of the peaks vary noticeably between the two spectra, probably because of a slight variation in pH, in a region where the tungstate chemistry is particularly sensitive to such variations.

Fig. 5 shows that very similar complexes form with molyb-

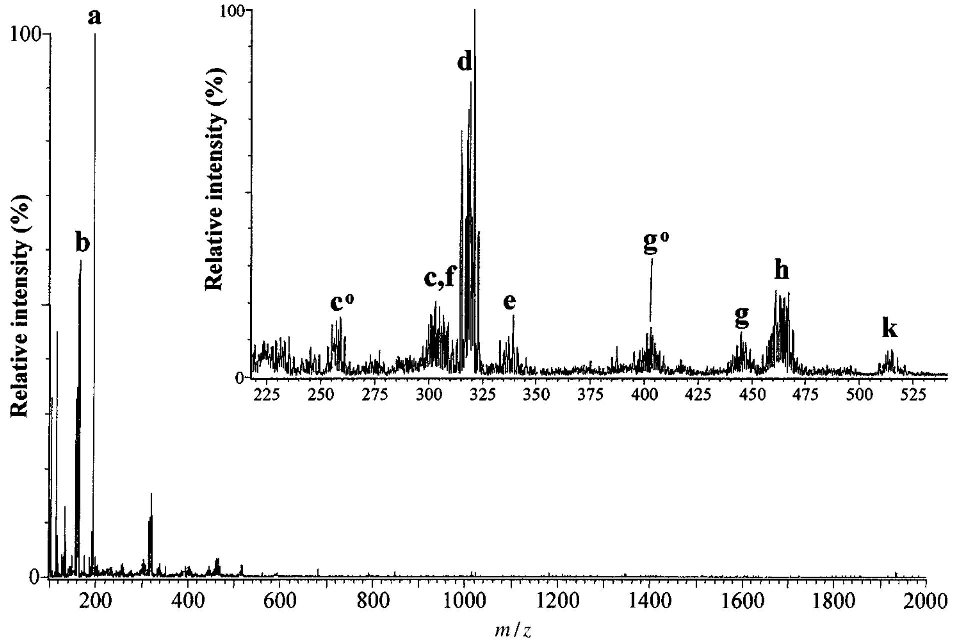

Fig. 5 Spectra as in Fig. 1(*a*), but starting with only lithium galacturonate and molybdate

Table 1 Species observed[a]

		acid H_5A:	gta	gta	gta	gta	gtu	gtu	gtu
		M:	W	W	Mo	Mo	W	W	Mo
Label	Species	Counter ion:	Li^+	Na^+	Li^+	Na^+	Li^+	Na^+	Li^+
a	$[H_4A]^-$		209	209	209	209	193	193	193
b	$[HMO_4]^-$		249	249	161	161	249	249	161
c°°	$[MO(A) - 2CO_2]^-$		(317)[b]	(317)	(229)	229			
c°	$[MO(A) - CO_2]^-$		(361)	(361)	273	273		(345)	257
c	$[MO(A)]^-$		405	405	317	317		(389)	301
d°	$[H_2MO_2A - CO_2]^-$				291	291			
d	$[H_2MO_2A]^-$		423	423	335	335	407	407	319
d′	$[LiHMO_2A]^-$		429		(341)				
d″	$[NaHMO_2A]^-$			445		357			
e	$[H_4MO_3A]^-$		(441)				425	425	337
e′	$[LiH_3MO_3A]^-$		447				(431)		
e″	$[NaH_3MO_3A]^-$			463				447	
f	$[HM_2O_7]^-$		481	481	305	305	(481)	481	(305)
f′	$[LiM_2O_7]^-$		(487)						
f″	$[NaM_2O_7]^-$							503	
g°°	$[M_2O_4A - 2CO_2]^-$		549	549	373	373			
g°	$[M_2O_4A - CO_2]^-$		(593)	(593)	417	417			401
g	$[M_2O_4A]^-$		637	637	461	461			445
h°°	$[H_2M_2O_5A - 2CO_2]^-$		(567)						
h°	$[H_2M_2O_5A - CO_2]^-$		(611)		435	435			
h	$[H_2M_2O_5A]^-$		655	655	479	479	639	(639)	463
h′	$[LiHM_2O_5A]^-$		661		485		(645)		
h″	$[NaHM_2O_5A]^-$			677		501		(661)	
i	$[H_3MA_2]^-$			(597)					
j	$[H_5MOA_2]^-$				(527)	(527)			
k	$[H_7MO_2A_2]^-$				545	545	601		513
k′	$[LiH_6MO_2A_2]^-$				551		607		
k″	$[NaH_6MO_2A_2]^-$					567			
l	$[H_9A_2]^-$		(419)	(419)			387		
l′	$[LiH_8A_2]^-$						393		393
l″	$[NaH_8A_2]^-$							409	
o	$[W_4O_{13}]^{2-}$						472		
p^{2-}	$[W_3O_{10}]^{2-}$						357		
p′	$[LiW_3O_{10}]^-$							719	
q	$[W_6O_{19}]^{2-}$						704	704	
r′	$[LiW_{10}O_{32}]^{3-}$						786.3		
s′	$[LiH_6W_{12}O_{41}]^{3-}$						959		
s″	$[NaH_6W_{12}O_{41}]^{3-}$							964.3	

[a] Noted by their *m*/*z* values. [b] Less secure assignments are in parentheses.

date, namely **c**, **d**, **e**, **g**, **h** and **k**. However, the only detectable molybdate oligomer at this pH is the dimer, **f**, because polymolybdates form less readily than polytungstates.[8]

The specific species identified above are listed in Table 1 for convenience.

Conclusion

The above study suggests answers to several key questions concerning the usefulness of ESI-MS for aqueous inorganic complexation chemistry.

Does the ESI-MS process alter the state of the solution species?

The answer to this question depends on whether or not account is taken of outer-sphere associations in the original solution. The gas-phase collisions, deliberately introduced in the initial cone acceleration, clearly serve to remove outer-sphere water from all the anions, so that many of them, such as **g** and **q**, end in a fully water-free state. Additional clustering of solvent water around the anions is only seen at very low cone voltages. Indeed, it is likely that passage through the gas phase also leads to limited dehydration and decarboxylation of the original anions. However, the CID and other results above show that such losses are not dominant, and that hydrated species also survive intact, over a wide range of cone voltages.

The phase transition also leads to protonated and metallated species, no doubt because these are favoured by the sudden drop in relative permittivity. However, it is likely that some loose attachment of alkali-metal ions does occur even in the solution phase, for the ^{183}W chemical shifts in most tungstate anions depend quite strongly on the Li^+ concentration of the ionic medium.[10] It is also likely that aqueous dinegative ions carry an ionic atmosphere of oxonium ions at or below neutral pH, that assists their protonation as they enter the gas phase.

Do the spectra give a semiquantitative representation of the anions present in solution?

Some mass and charge selection effects are almost unavoidable in mass spectra, particularly reductions of intensity at higher values of *m*/*z*. Nevertheless, the present spectra correspond quite closely to what would have been predicted from the earlier NMR data, given the above caveats. No expected species are absent.

Do new species arise in the final stages of droplet evaporation?

The acid dimers and oligomers noted above do not necessarily represent species present in dilute solution. They could be artefacts of the high concentrations pertaining at the final stages of evaporation. Alkali-metal halide solutions are well known to form charged clusters of this type, for they are commonly used as mass markers. However, we have only found such clusters to arise from solutions whose initial concentration is appreciably higher than the present ones. They are also observed with *e.g.* molybdates, at 10^{-2} mol dm^{-3} and above, where they tend to give weak, monotonic series of anion types such as $[LiMO_4(MO_3)_n]^-$, that decay slowly in intensity with increasing *n*. Such series are not seen in the present spectra. For example, although Fig. 4(*a*) reveals several tungstate oligomers, including W_6 and W_{12} anions, it shows no clear W_5, W_7 or W_{8-11} species. Similarly, no complexes of type $[X(HX)]^-$ or $[X_2]^{2-}$ are seen, despite the availability of carboxylate groups to assist in the formation of hydrogen-bonded dimers. It is likely that non-specific clustering can be routinely suppressed by working with sufficiently dilute solutions, *e.g.* millimolar or less, and especially if ligands are present to compete with any clustering process. Further, quantitative study of the effects of dilution on the spectra would now be desirable.

Thus, ESI-MS shows considerable promise for the rapid, semiquantitative assessment of anionic speciation in dilute, complex aqueous solutions, particularly those whose other properties make them problematic for *e.g.* NMR or potentiometric study.

Acknowledgements

We thank ICI and Micromass U.K. for funding M. J. D.

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Received 10*th March* 1998; *Paper* 8/01944D