Electrospray Tandem Mass Spectrometry of Polyoxoanions

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A number of polyoxomolybdates and polyoxotungstates are studied by means of electrospray tandem mass spectrometry; in each case, the mass spectrum of a solution of the polyoxoanion shows the polyoxoanion as the base peak with a minimal degree of fragmentation.

The chemistry of polyoxoanions has attracted much attention in recent years because of its potential applications to a wide range of catalytic processes.[1] Due to the complexity of many polyoxoanions, it is often difficult to obtain accurate analytical and molecular mass data for them. Fast atom bombardment mass spectrometry (FABMS) has been found useful for the determination of the elemental compositions and molecular masses of a number of polyoxoanions.[2,3] However, polyoxoanion salts have limited solubility in the glycerol and thioglycerol matrices used in FAB. Furthermore, rather substantial fragmentation of some polyoxoanions was observed.[2,3] Recently, electrospray mass spectrometry (ESMS) has become the soft ionization/desorption technique of choice and has proven to be invaluable in the study of biomacroions such as proteins and oligonucleotides.[4] It is a softer technique than FAB, and serves to transfer/desorb ions from solution to the gas phase with minimal fragmentation along the ion path. To investigate if ESMS is also useful for the study of large cluster ions such as polyoxoanions, we studied a number of polyoxomolybdates and polyoxotungstates of different compositions and structures.

The polyoxoanions studied in this work, together with their mass spectral data are shown in Table 1.† The theoretical *m*/*z* values reported are those of the most abundant peak within each isotopic mass distribution of the ions divided by the ion charge while the observed *m*/*z* values are those measured from the centroid of the electrospray mass spectral distribution. In every case, little or no fragmentation was observed and there was good agreement between the experimental and calculated values (see Fig. 1). The mass spectra of the tetrabutylammonium salts of the polyoxoanions in acetone show the polyoxoanions as the base peak, no solvated ions being observed under our typical declustering conditions.[5,6] The mass spectrum of $H_3PW_{12}O_{40}P{\cdot}xH_2O$ in either acetone or 50/50 water–methanol shows only the completely deprotonated ion, $[PW_{12}O_{40}]^{3-}$; this is expected since the acid is known to be completely dissociated in aqueous solution.[1] The compound $H_4SiMo_{12}O_{40}{\cdot}xH_2O$ is also known to be tetrabasic[1] with all pK_as < 2. However, for this analyte, the mass spectra in acetone and in methanol reveal the presence of $[SiMo_{12}O_{40}]^{4-}$ and $[HSiMo_{12}O_{40}]^{3-}$ in the ratio of approximately 5 : 3; addition of 20% water to the methanol appears to encourage deprotonation and shifts the ratio to 4 : 1. The spectrum of $Na_4SiW_{12}O_{40}{\cdot}5H_2O$ in methanol shows the ion, $[SiW_{12}O_{40}]^{4-}$, with *ca.* 10% $[NaSiW_{12}O_{40}]^{3-}$.

Table 1 Electrospray mass spectral data for polyoxoanions[a]

Compound	Ion	Theoretical *m*/*z*	Observed *m*/*z*
$[Bu^n_4N]_2[Mo_2O_7]$[b]	$[Mo_2O_7]^{2-}$	152	152
$[Bu^n_4N]_2[Mo_6O_{19}]$[b]	$[Mo_6O_{19}]^{2-}$	440	440
$[Bu^n_4N]_2[W_6O_{19}]$[b]	$[W_6O_{19}]^{2-}$	704	704
$[Bu^n_4N]_4[Mo_8O_{26}]$[b]	$[Mo_8O_{26}]^{4-}$	296	296
$[Bu^n_4N]_4[W_{10}O_{32}]$[b]	$[W_{10}O_{32}]^{4-}$	588	588
$[H_3PW_{12}O_{40}]{\cdot}xH_2O$[c]	$[PW_{12}O_{40}]^{3-}$	959	959
$[H_4SiMo_{12}O_{40}]{\cdot}xH_2O$[c]	$[HSiMo_{12}O_{40}]^{3-}$	607	608
	$[SiMo_{12}O_{40}]^{4-}$	455	455
$Na_4[SiW_{12}O_{40}]{\cdot}5H_2O$[c,d]	$[SiW_{12}O_{40}]^{4-}$	718	719
	$[NaSiW_{12}O_{40}]^{3-}$	965	966

[a] All spectra were collected in the negative ion detection mode. Solutions were *ca.* 1 mmol dm^{-3} in acetone. [b] Prepared according to ref. 7. [c] Obtained from Strem Chemicals. [d] Spectrum obtained from *ca.* 1 mmol dm^{-3} analyte in methanol.

Table 2 shows the fragment ions of a number of polyoxoanions after collision-induced dissociation (CID). The CID of $[Mo_2O_7]^{2-}$ shows the ions, $[MoO_4]^-$ and $[MoO_3]^-$, at approximately the same abundance, which is in accordance with the two fragment ions being produced from the cleavage of a bridging Mo–O bond of the precursor ion, $[O_3Mo{-}O{-}MoO_3]^{2-}$. A similar fragmentation pattern has also been observed for the ion, $[Cr_2O_7]^{2-}$.[6] The CID of $[W_6O_{19}]^{2-}$, $[W_{10}O_{32}]^{4-}$, $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$ all show fragment ions due to multiple losses of WO_3 or MoO_3 units. Assignments of the fragment ions originating from the quadruply charged precursor ions are not unambiguous because of the uncertainty of the fragment ions' charges. For example, the fragment ion at *m*/*z* 356 of the precursor $[W_{10}O_{32}]^{4-}$ can be assigned as both $[W_3O_{10}]^{2-}$ (as shown in Table 2) or $[W_6O_{20}]^{4-}$ and that at *m*/*z*

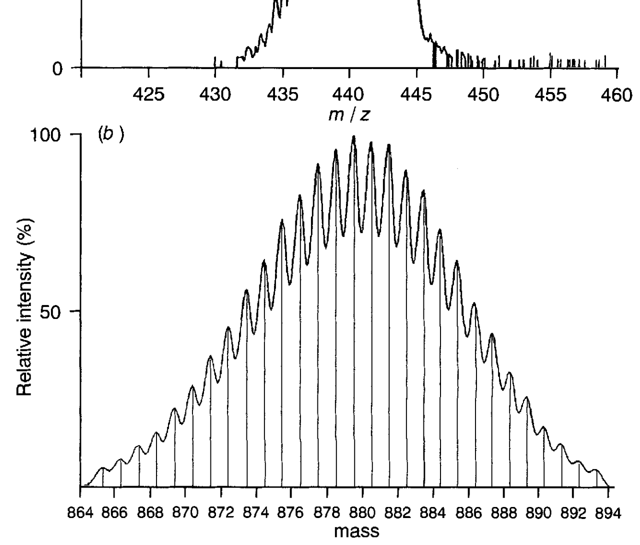

Fig. 1 $[Mo_6O_{19}]^{2-}$ (*a*) electrospray mass spectrum; (*b*) calculated isotopic distribution of the ion. Note that the isotopic separation in the mass spectrum is *ca.* 0.5 *m*/*z* units, the signature of a doubly charged ion.

471 of the same precursor can likewise be assigned as both $[W_4O_{13}]^{2-}$ or $[W_8O_{26}]^{4-}$; the fragments are assigned as doubly charged in Table 2 because of the absence of $[W_7O_{23}]^{4-}$ (*m*/*z* 414) and $[W_9O_{29}]^{4-}$ (*m*/*z* 530), and the presence of *m*/*z* 704, $[W_6O_{19}]^{2-}$, which is complimentary to $[W_4O_{13}]^{2-}$, and that of *m*/*z* 819, $[W_7O_{22}]^{2-}$, which is complimentary to $[W_3O_{10}]^{2-}$. The CID of $[PW_{12}O_{40}]^{3-}$ yields the ion, $[PW_9O_{26}]^{3-}$ by the loss of W_3O_{14}, which is probably one of the groups of three edge-shared octahedra in the Keggin structure.[1] The CID of $[SiMo_{12}O_{40}]^{4-}$ and $[SiW_{12}O_{40}]^{4-}$, however, give fragment ions due to different apparent losses of M_xO_y. $[SiMo_{12}O_{40}]^{4-}$ yields the fragment ions, $[SiMo_{10}O_{30}]^{4-}$, $[SiMo_8O_{24}]^{4-}$ and $[SiMo_6O_{18}]^{4-}$ with sequential losses of formally Mo_2O_{10}, Mo_2O_6 and Mo_2O_6, respectively. The fragmentation pattern of $[SiW_{12}O_{40}]^{4-}$ parallels that of $[SiMo_{12}O_{40}]^{4-}$ (Table 2).

In conclusion, electrospray mass spectra of high molecular mass polyoxoanions can readily be obtained with apparently little or no sign of degradation. ESMS is thus a potentially valuable technique for the characterization and study of the solution chemistry of polyoxoanions.

Financial support to T. C. L. from the Research Grants Council and the City University of Hong Kong is gratefully acknowledged.

Received, 29th December 1994; Com. 4/07860H

Table 2 Fragment ions of polyoxoanions

Precursor ions (*m*/*z*)[a,b]	Fragment ions [*m*/*z*,[b] relative abundance (%)]	E_{lab}[c]/eV
$[Mo_2O_7]^{2-}$ (152)	$[MoO_3]^-$ (143, 3.7); $[MoO_4]^-$ (160, 3)	160
$[Mo_6O_{19}]^{2-}$ (440)	$[Mo_5O_{16}]^{2-}$ (369, 0.1); $[Mo_4O_{13}]^{2-}$ (297, 3.1); $[Mo_3O_{10}]^{2-}$ (224, 1.3); $[Mo_2O_7]^{2-}$ (152, 0.1)	80
$[W_6O_{19}]^{2-}$ (704)	$[W_4O_{13}]^{2-}$ (471, 3.1); $[W_3O_{10}]^{2-}$ (356, 6.2)	80
$[Mo_8O_{26}]^{4-}$ (296)	$[Mo_6O_{20}]^{4-}$/$[Mo_3O_{10}]^{2-}$ (224, 19); $[Mo_4O_{14}]^{4-}$/$[Mo_2O_7]^{2-}$ (152, 2)	160
$[W_{10}O_{32}]^{4-}$ (588)	$[W_4O_{13}]^{2-}$ (471, 9); $[W_3O_{10}]^{2-}$ (356, 7); $[W_6O_{19}]^{2-}$ (704, 5); $[W_7O_{22}]^{2-}$ (819, 2)	160
$[PW_{12}O_{40}]^{3-}$ (959)	$[PW_9O_{26}]^{3-}$ (702, 2)	300
$[SiMo_{12}O_{40}]^{4-}$ (455)	$[SiMo_{10}O_{30}]^{4-}$ (367, 14); $[SiMo_8O_{24}]^{4-}$ (296, 37); $[SiMo_6O_{18}]^{4-}$ (223, 5)	160
$[SiW_{12}O_{40}]^{4-}$ (719)	$[SiW_{10}O_{30}]^{4-}$ (588, 1.7); $[SiW_8O_{24}]^{4-}$ (472, 3); $[SiW_6O_{18}]^{4-}$ (354, 0.6)	320

[a] 100% abundance. [b] Centroid of the distribution. [c] Average number of collisions = 1.

Footnote

† Experiments were performed on a SCIEX TAGA Model 6000E triple quadrupole mass spectrometer, which has an upper limit of *m*/*z* *ca.* 1400. For details of the set-up see ref. 5.

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