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Applications of Laser Desorption and Electrospray Ionization Mass Spectrometry at the Transition between Clusters and Colloids

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The development of powerful new mass spectrometric techniques such as electrospray ionization (ESI)[1] and matrix-assisted laser desorption ionization (MALDI)[2] has been driven by the polymer and biological sciences. Workers in other areas, for whom conventional techniques are less useful, such as cluster chemistry, are now embracing these ionization methods. The mass spectrometric characterization of high-nuclearity metal carbonyl clusters using more traditional techniques is not trivial because of the high mass of clusters, their relative involatility, and their thermal sensitivity. Recently, ESI has been applied to cluster molecules.[3] This technique provides a straightforward and superior determination of molecular weights for these compounds, in contrast to laser desorption ionization (LDI), which tends to give much more complicated spectra.[4] In this communication we compare LDI and ESI mass spectrometry for measuring the molecular weights of large anionic osmium clusters.

It has previously been shown that the laser desorption/ionization of neutral metal carbonyl clusters can lead to the generation of high molecular weight clusters and supraclusters.[4] Similar phenomena have been observed using ^{252}Cf plasma desorption[5] and electron impact Fourier transform ion cyclotron resonance mass spectrometry.[6] Nevertheless, we have found that LDI mass spectrometry may be used for molecular weight determination of anionic clusters. Here, little or no supraclustering is observed and the spectra consist mainly of peaks attributable to the parent ion and to fragment ions derived from the sequential loss of carbonyl ligands. Information unavailable routinely by other techniques, i.e., the molecular weight of a cluster directly from the solid phase and, in certain cases, a count of the carbonyl groups present (vide infra), is provided. To illustrate the use of this technique, the negative-ion LDI-TOF mass spectrum of $[PPN]_2[Os_{10}C(CO)_{24}]$ (PPN = Ph_3PNPPh_3)[7] at moderate laser power is shown in Figure 1.[8] The highest mass peak at *m*/*z* 2588 corresponds to $[Os_{10}C(CO)_{24}]^-$, and the peaks at lower mass correspond to the ions $[Os_{10}C(CO)_n]^-$ ($n = 5-23$). Higher laser power caused further CO stripping to give eventually the naked metal core, $[Os_{10}C]^-$, whereas lower laser power brought about an increase in the abundance of the molecular ion. CO loss fragments are always observed, even at threshold laser power. No doubly charged ions were observed for this sample or in any of the other samples studied. Electron loss from the cluster is an entirely expected reaction in the ion plume during ablation by the laser, and in our previous LDI studies of clusters[4] we have only observed singly charged ions.

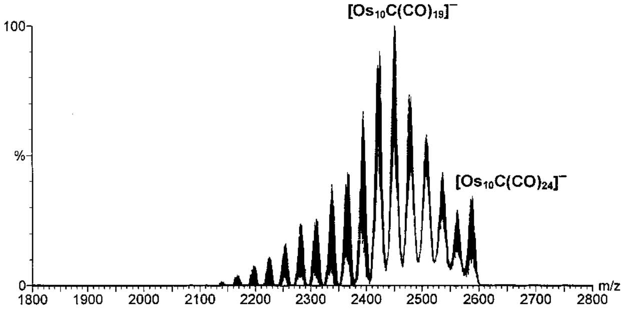

Figure 1. Negative-ion LDI-TOF mass spectrum from $[PPN]_2[Os_{10}C(CO)_{24}]$.

The ESI mass spectrum of $[Os_{10}C(CO)_{24}]^{2-}$ at a low cone voltage shows a single envelope of peaks due to the intact, doubly

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(8) Low-resolution LDI-TOF mass spectra were obtained using a Kratos Kompact MALDI-4 instrument in linear mode. High-resolution data were recorded on $[PPN]_2[Os_{10}C(CO)_{24}]$ using a TOFSpec2E instrument in reflectron mode. Dilute dichloromethane solutions of the clusters were evaporated directly onto the sample slide (no matrix was used). The laser power was typically modulated to maximize the signal-to-noise ratio. In all cases the machines were run in negative-ion mode.

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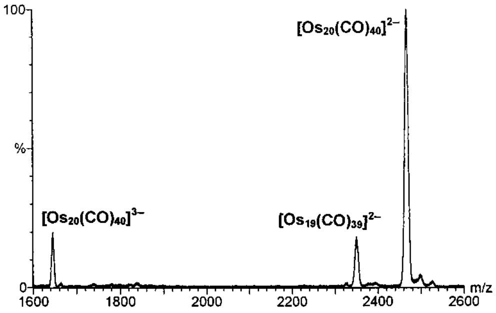

Figure 2. Negative-ion electrospray mass spectrum of a mixture of osmium HNCC anions.

charged molecular ion.[3e] Application of energy-dependent electrospray ionization (EDESI)[9] to this compound results in stripping of the CO ligands and the appearance of peaks corresponding to $[Os_{10}C(CO)_n]^{2-}$ ($n = 5-24$). The LDI and EDESI spectra provide similar information with regard to molecular weight and structure. No species attributable to fragmentation of the cluster core were observed using either technique.

A number of other cluster anions were also investigated using LDI-MS, including the known large dianionic tetrahedral cluster $[Os_{20}(CO)_{40}]^{2-}$.[10] The broad green-brown band obtained from the silica plate after chromatography of a mixture containing $[PPN]_2[Os_{20}(CO)_{40}]$ was deposited directly onto the sample probe, and a spectrum was generated that shows a peak for the intact parent ion as well as the CO loss peaks $[Os_{20}(CO)_n]^-$ ($n = 19-40$) in the range m/z 4338−4926.

One of the main assets of the LDI technique, viz. extensive CO loss fragments, also turns out to be one of the major drawbacks because it can potentially obscure other compounds present. Examination of the same sample of $[Os_{20}(CO)_{40}]^{2-}$ using ESI mass spectrometry[11] also reveals an intact parent ion for this cluster (see Figure 2) in which there are no fragments produced. In addition, however, there are other notable features in the spectrum, principally the presence of two other compounds that can be confidently formulated as $[Os_{20}(CO)_{40}]^{3-}$ and $[Os_{19}(CO)_{39}]^{2-}$ (other, unidentified species are also observed in trace amounts). The presence of a mixture of components reflects the problems associated with the crystallization of $[Os_{20}(CO)_{40}]^{2-}$ used to obtain the X-ray structure.[12] Repeating the preparation gave different proportions of the various ions. There was no evidence to suggest that either $[Os_{20}(CO)_{40}]^{3-}$ or $[Os_{19}(CO)_{39}]^{2-}$ was derived from $[Os_{20}(CO)_{40}]^{2-}$ in the mass spectrometer because changing experimental parameters such as the solvent or the desorption temperature had little effect on the spectrum. Increasing the cone voltage resulted only in the stripping of carbonyl ligands, and fragmentation of the metal core was never observed, in keeping with previous studies of cluster compounds by electrospray ionization mass spectrometry.[3e,9]

The observed cluster valence electron (cve) count for $[Os_{20}(CO)_{40}]^{2-}$ (242) does not fit with the values of 254 [13] and 252 [14] predicted for a cluster unit with a cubic close-packed M_{20} metal core (Figure 3a). An explanation for this difference was subsequently provided.[10] Predicting the structure of $[Os_{20}(CO)_{40}]^{3-}$ is clearly not a trivial exercise, but since the dianion could, at least in principle, accommodate additional electron density, it is not unreasonable to assume that it has a closely related tetrahedral cubic close-packed metal core. The most rational structure for this compound is that in which an apical osmium has been removed from $[Os_{20}(CO)_{40}]^{2-}$ (see Figure 3b). A related example in which two clusters with large tetrahedral cubic close-packed structures that differ by decapping at an apex comprises $[Ni_{37}Pt_4(CO)_{46}]^{6-}$ and $[Ni_{36}Pt_4(CO)_{45}]^{6-}$.[15] Similar to the high-nuclearity osmium clusters, these nickel−platinum clusters are obtained together with a wide range of other large clusters and represent another series of reaction products that may benefit from an ESI analysis.

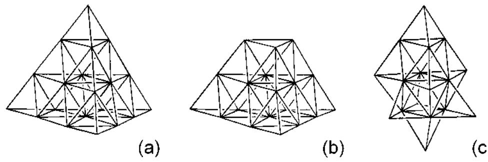

Figure 3. Metal core structures of (a) $[Os_{20}(CO)_{40}]^{2-}$, (b) $[Os_{19}(CO)_{39}]^{2-}$ (postulated), and (c) $[Os_{17}(CO)_{36}]^{2-}$.

The drastically different metal atom topology of $[Os_{17}(CO)_{36}]^{2-}$ (Figure 3c) could imply that the simple "decapping" model such as the one used here may be too simplistic. However, the ESI study has provided new information unavailable by other methods and experiments are now in hand to try to isolate and fully characterize the new clusters.

Clusters with nuclearities around 20 are not far from being considered colloidal in size. Much effort has been devoted to defining and distinguishing the interface between that which constitutes a cluster and a colloid.[16] It is well-known that colloids often contain poorly defined metal polyhedra and their nuclearities and charges are often not as precise as those of clusters. By use of this criterion, the mixture of osmium components observed here could be considered colloidal, especially given that the trianionic species may not necessarily have the same structure as the dianionic species. As such, there is no real difference between colloids and clusters, and a colloid simply becomes a cluster once it has been characterized by X-ray crystallography. With the insights gained from the ESI mass spectrometry study of $[Os_{20}(CO)_{40}]^{2-}$, caution must still be applied because an X-ray structure may not necessarily represent the true identity of the bulk sample. With these high-nuclearity compounds most spectroscopic and analytical techniques do not shed any light on their purity and ESI seems to be the most informative technique available, and the successful application of LDI-MS to compounds of this type has added another characterization method that may be used by workers studying compounds at the transition between clusters and colloids.

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Supporting Information Available: Negative-ion EDESI mass spectrum of $[PPN]_2[Os_{10}C(CO)_{24}]$ and negative-ion ESI spectrum from a rechromatographed sample of $[PPN]_2[Os_{20}(CO)_{40}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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