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GENERATION OF $\text{Au}_2\text{Cl}_{2n+1}$ ($n = 1-3$) CLUSTER IONS BY LASER DESORPTION/IONIZATION MASS SPECTROMETRY

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ABSTRACT

Gold chloride clusters were generated from an aqueous solution of gold-hydrochloric acid deposited onto the target plate using laser desorption/ionization (LDI) on a commercial matrix assisted laser desorption/ionization – time of flight (MALDI-TOF) mass spectrometric instrument. In our experimental conditions negative mode of LDI mass spectra provided the most valuable informations. The mass peaks at m/z about 339, 499, 571, 641, were assigned to AuCl_4^- , Au_2Cl_3^- , Au_2Cl_5^- , Au_2Cl_7^- cluster ions, respectively. The Au_2Cl_5^- and Au_2Cl_7^- clusters are detected for the first time in this work. This research showed that LDI MS, thanks to its easy experimental procedure, a soft ionization technique which may be a useful characterization tool in the chemistry of heterogeneous gold clusters.

INTRODUCTION

Investigations of homogeneous and heterogeneous clusters of gold are important for their potential application in different areas such as catalysis, optics, medicaments, and environmental sciences [1-4]. For specific technological and scientific requests, it is necessary to examine the structure and stability of these clusters as the function of their composition and size. Generally, mass spectrometric methods allow both the examination of conditions for obtaining various types of metal clusters, and the investigation of their electronic and geometric properties. In the past two decades, several mass spectrometric techniques have been used to study homogeneous gold clusters, and most of these techniques were based on the evaporation of metals by heating, or using laser ablation and ion-bombardment. For example, laser desorption Fourier-transform ion cyclotron resonance (LD FT-ICR) mass spectrometry was used as a simple method for generating large gold cluster ions, $\text{Au}_n^{+/-}$ [5]. Mass distributions

of negative cluster ions of gold $(\text{Au})_n^-$ obtained by the bombardment of metal sheets with Xe ions were examined up to cluster size $n = 250$ [6].

Research of the structures of gold halides clusters is important because it provides insight into the extent of aurophilic interactions which are intermediates between van der Waals' forces and covalent bonding. Previous studies have shown that Au_2Cl_3^+ , Au_2Cl_4^+ , and Au_2Cl_6^+ clusters can be obtained by the evaporated HAuCl_4 at 100–120°C, and these species were detected in the conventional way through electron impact ionization (EI) [7]. Also, mononuclear cluster types $[\text{AuCl}_2]^+(\text{H}_2\text{O})_n$ ($n = 0-4$), $[\text{AuOHCl}]^+(\text{H}_2\text{O})_n$ ($n = 0-1$) and $[\text{AuCl}_2]^+(\text{HCl})_2(\text{H}_2\text{O})_n$ ($n = 0-4$), and dinuclear cluster types $[\text{Au}_2\text{Cl}_{5-x}(\text{OH})_x]^+(\text{H}_2\text{O})_n$ ($x = 0-1$) have been detected in electrospray ionization mass spectra of aqueous AuCl_3 [8].

In this work, we have investigated the conditions for the application of LDI TOF mass spectrometry for the generation of gold chloride clusters from an aqueous solution of gold-hydrochloric acid.

EXPERIMENTAL

LDI mass spectra were obtained using the commercial MALDI-TOF mass spectrometer (Voyager-DE PRO, AB Sciex, USA) equipped with a 20 Hz pulsed nitrogen laser (337 nm) and with delayed extraction. A stainless steel target was used as the MALDI substrate on which the samples are deposited. The accelerating voltage used was 19 kV. The mass spectra were collected using both positive and negative ion modes and both linear and reflector modes. Data Explorer software 4.9 includes a suite of tools and processing options that allow you to graphically and interactively manipulate mass spectral data (for example, determine elemental composition, theoretical isotope distributions, resolution, signal-to-noise ratio, and fragment ions). No matrices were used for this sample preparation. A small volume (0.5 μl) of an aqueous HAuCl_4 solution, concentration 2.5 g Au/dm^3 , was applied onto the sample plate and left to dry at room temperature.

RESULTS AND DISCUSSION

In our experimental conditions the positive mode LDI mass spectra did not contain the peaks of Au-Cl clusters. The positive mode spectra did confirm the identity of the Au_n^+ ($n = 1-3$) clusters, however these clusters have already been detected. For that reason, positive mode of LDI mass spectrum is neither presented nor further discussed.

An example of a mass spectrum for aqueous solution of gold-hydrochloric acid obtained in the reflector negative mode is shown in Fig. 1.

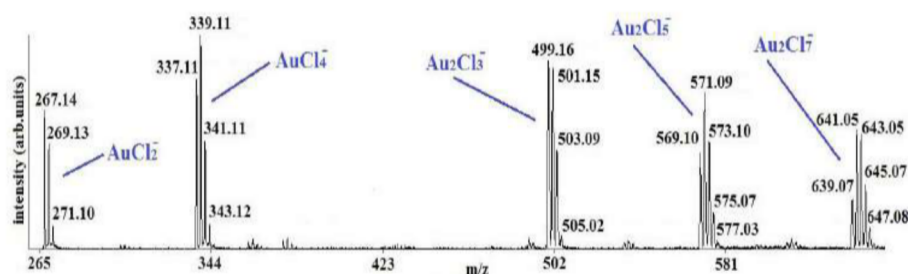


Figure 1. Reflector negative ion LDI-TOF mass spectrum of HAuCl_4 . The spectrum represents the average of 300 laser shots with laser intensity of 1800 a.u.

For the confirmation of the identity of signals detected, we have compared experimental and theoretical values of gold chloride clusters generated via LDI TOF mass spectrometry, in Table 1. The experimental values have a very good agreement with theoretical values of m/z ratio, which confirms the identity of signals detectable in the LDI spectra.

Table 1. Experimental values of $\text{Au}_2\text{Cl}_{2n+1}$ ($n = 1-3$) generated via laser desorption/ionization-time of flight mass spectrometry (theoretical isotope distributions were taken from Data Explorer software 4.9)

Cluster	Experimental m/z	Theoretical m/z	Relative intensity of isotopes (%)	Cluster	Experimental m/z	Theoretical m/z	Relative intensity of isotopes (%)
Au_2Cl_3^-	499.16	498.84	100	Au_2Cl_7^-	639.07	638.72	44
	501.15	500.84	97		641.05	640.71	100
	503.09	502.84	31		643.05	642.71	97
	505.02	504.83	3		645.07	644.71	52
Au_2Cl_5^-	569.10	568.78	62		647.08	646.70	17
	571.09	570.77	100				
	573.10	572.77	65				
	575.07	574.77	21				
	577.03	576.77	3				

These data show that negative ion of cluster Au_2Cl_3^- is the dominant dinuclear gold cluster, in which gold exists as the monovalent (Au^{I}) ion, while Au_2Cl_5^- cluster contains monovalent (Au^{I}) and trivalent (Au^{III}) ions, and Au_2Cl_7^- cluster contains two trivalent (Au^{III}) ions. It should be observed

that in the EI mass spectra only positively charged clusters, such as Au_2Cl_3^+ , Au_2Cl_4^+ , and Au_2Cl_6^+ (with different oxidation state of gold than above mentioned) have been detected after HAuCl_4 has evaporated at a small rate ($\sim 3\text{--}5$ K/min) [7]. In our case, heating of the sample (HAuCl_4) in the ionization chamber was very fast, because desorption/ionization process is determined by the energy density supplied to the sample by the laser pulse. In the LDI mass spectrum (Fig. 1) only negatively charged clusters were detected. This indicates that heating rate of the sample may affect on stability, composition, and size of dinuclear gold chloride clusters.

CONCLUSION

Here, the laser desorption/ionization – time of flight (LDI-TOF) mass spectra of aqueous solution of gold-hydrochloric acid have been investigated. Mass spectra were acquired in both linear and reflector positive/negative modes. However, the best resolution of isotope peaks of $\text{Au}_2\text{Cl}_{2n+1}$ ($n = 1\text{--}3$) clusters were obtained in reflector negative ion mode. Some of the clusters were found for the first time whose isotope peaks were in very good correlation with theoretical values.

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