Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS) of Rhenium(III) Halides: A Characterization Tool for Metal Atom Clusters

Nancy Carter Dopke, Paul M. Treichel,* and Martha M. Vestling

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received September 24, 1997

The laser desorption/ionization (LDI) and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of trinuclear $Cs_3Re_3Cl_{12}$ and $Cs_3Re_3Br_{12}$ and dinuclear $(Bu_4N)_2[Re_2Cl_8]$ are reported. In each case, characteristic fragments due to the loss of halogen atoms give ion signals that can be used to identify the number of rhenium atoms and the identity of ligands bound to the cluster. The ion signals are identified by both *m/z* values and distinctive isotope patterns. The results presented here illustrate the usefulness of MALDI-TOF mass spectrometry in the characterization of metal atom clusters.

Introduction

The rhenium(III) clusters are attractive systems for investigation of rational low-temperature pathways for the synthesis of new metal atom clusters. Both the dinuclear and trinuclear rhenium(III) halides are commercially available as starting materials. In addition, stable compounds with 1, 2, 3, and 6 rhenium atoms are known. The interconversion of these known species is an intriguing challenge. Historically, trinuclear species are of particular interest. The recognition of the structure of $[Re_3Cl_{12}]^{3-}$ and the existence of multiple metal bonds between the rhenium atoms in rhenium(III) halide cluster compounds greatly contributed during the early development of the metal atom cluster field. The chemistry of trinuclear rhenium(III) halides has been reviewed, and many derivatives have been identified.[1]

In previous studies in this area the characterization of polynuclear rhenium(III) halide derivatives has relied primarily on elemental analysis, UV−visible spectroscopy, and X-ray crystallography. While these techniques have been used routinely, each has some disadvantages. Elemental analysis has been used for almost all of the compounds, but these data are often not definitive and no structural information is available. UV−vis spectra have been used to confirm that the trinuclear nature is retained in the products of reactions of $(Re_3X_9)_n$ (X = Cl, Br) with neutral donor ligands and anionic ligands.[2−6] Shifts in the absorbance bands can be attributed to different ligands on the complex, but explicit identification of the ligands from these data is not easily made. X-ray crystallography has been the most valuable technique in providing detailed structural information on these compounds,[7] but the growth of suitable crystals is often a time-consuming and not always successful endeavor. It would be advantageous to have a quick, simple characterization tool that would provide information concerning the identity of ligands as well as the nuclearity of the species. NMR and IR spectroscopies, widely used in the characterization of metal complexes, have been of use only in those specific cases in which the ligands provide characteristic spectra.

In order for mass spectrometry to provide useful molecular weight information, analytes need to be in the gas phase and ionized. Electron impact (EI) ionization has been widely and successfully used in the analysis of inorganic species that are volatile and thermally stable. The EI mass spectrum of rhenium trichloride vapor from the polymer $(Re_3Cl_9)_n$ was reported in the 1960's.[8] The positive ion $[Re_3Cl_9]^+$ was the most abundant species, and chlorine loss and fragmentation to species with fewer rhenium atoms were reported. However, EI cannot be used for involatile species and ionic compounds. Thus, many derivatives of $(Re_3Cl_9)_n$, such as $Cs_3Re_3Cl_{12}$, are specifically excluded from EI mass spectrometric analysis.

Developments in ionization techniques have now made it possible to use mass spectrometry to analyze such species. Fast atom bombardment (FAB) and liquid secondary ion mass spectrometry (LSIMS) have been established as valuable techniques in the analysis of involatile and/or thermally labile compounds. FAB and LSIMS suffer from the problem of chemical noise (referred to as peak-at-every-mass or incoherent fragmentation).[9] Our preliminary attempts to obtain FAB mass spectra of $Cs_3Re_3Cl_{12}$ were unsuccessful. In recent years electrospray ionization (ESI) has been successfully applied to the analysis of inorganic species.[10] In this technique pre-existing ions are transferred from solution to gas phase for analysis. A prerequisite is that the analyte must be soluble and non-reactive in the chosen sprayable solvent.

Matrix-assisted laser desorption/ionization (MALDI) is one of the latest laser ionization methods used in the mass

---

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms,* 2nd ed.; Clarendon Press: Oxford, 1993.

(2) Robinson, B. H.; Fergusson, J. E. *J. Chem. Soc.* **1964**, 5683.

(3) Hickford, J. H.; Fergusson, J. E. *J. Chem. Soc. A* **1967**, 113.

(4) Fergusson, J. E.; Hickford, J. H. *Inorg. Chim. Acta* **1968**, *2,* 475.

(5) Gutmann, V.; Paulsen, G. *Monatsh. Chem.* **1969**, *100,* 358.

(6) Cameron, C. J.; Wigley, D. E.; Wild, R. E.; Wood, T. E.; Walton, R. A. *J. Organomet. Chem.* **1983**, *255,* 345.

(7) See, for example: Meyer, G.; Irmler, M. *Z. Anorg. Allg. Chem.* **1990**, *587,* 197.

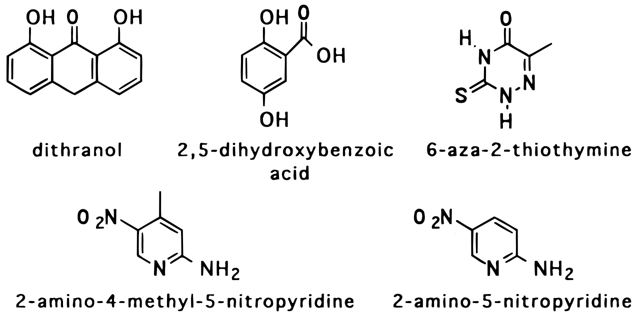
(8) (a) Rinke, K.; Schäfer, H. *Angew. Chem., Int. Ed. Engl.* **1965**, *4,* 148. (b) Büchler, A.; Blackburn, P. E.; Stauffer, J. L. *J. Phys. Chem.* **1966**, *70,* 685.

(9) Fenselau, C.; Cotter, R. J. *Chem. Rev.* **1987**, *87,* 501.

(10) Colton, R.; D'Agostino, A.; Traeger, J. C. *Mass Spectrom. Rev.* **1995**, *14,* 79.

S0020-1669(97)01220-2 CCC: $15.00

Chart 1. Structures of Compounds Used as Matrices for MALDI-TOF MS



spectrometric analysis of involatile compounds.[11] Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) has been extensively utilized for the analysis of large involatile biomolecules[12] and polymers.[13] However, there are few reports of its use in the analysis of inorganic species and none of these deal with metal atom clusters.[14]

In MALDI-TOF MS the analyte is embedded in a solid matrix, usually a small highly absorbing organic molecule (Chart 1). Typically the sample is deposited on a target as a solution of the matrix and analyte and then allowed to air dry before the target is inserted into the mass spectrometer, which is under vacuum. The excitation of the matrix by pulsed laser light results in the desorption and ionization of intact molecular ions. The charged species are then propelled into the flight tube where they are separated on the basis of mass. MALDI-TOF MS is a simple and fast technique that requires very little sample, does not require the compound to be in solution (the analyte could be deposited as a slurry), and allows detection of intact molecular ions with masses in excess of 100 000 Da. The lower limit of the practical detection range is restricted only when matrix peaks hide ion signals in the region of interest, but this can be controlled by changing to a matrix that does not produce ion signals in that region.

Due to the ease and potential for detecting molecular ions, we felt that MALDI-TOF MS would be a useful characterization tool in our studies of rhenium(III) halides. In this paper we report the laser desorption ionization (LDI) and matrix-assisted laser desorption/ionization (MALDI) mass spectra of four anionic rhenium(III) species: $Cs_3Re_3Cl_{12}$, $Cs_3Re_3Br_{12}$, $(Bu_4N)_2Re_2Cl_8$, and $(Et_4N)[Re_3Cl_{10}(H_2O)_2]$. In looking for the optimum conditions, different matrices were investigated, and the effects of varying the concentration of the analyte and laser power were evaluated.

Experimental Section

Instrumental. Mass spectra with (MALDI) and without (LDI) a matrix were collected on a Bruker Reflex II TOF-MS equipped with a N_2 laser. For spectra of negative ions an accelerating voltage of −20 kV and a reflectron voltage of −21.2 kV were used. For spectra of positive ions an accelerating voltage of 25 kV and a reflectron voltage of 26.25 kV were used. All spectra were taken in the reflectron mode with the laser power just above the threshold of ion formation/desorption, except as noted in the discussion. Both negative and positive mode spectra were recorded and analyzed. Spectra are typically the sum of 50 laser shots.

The matrices chosen for this study were 2,5-dihydroxybenzoic acid (DHB),[15] dithranol (1,8-dihydroxy-9-anthrone),[14a] 6-aza-2-thiothymine (aTT),[16] 2-amino-4-methyl-5-nitropyridine (AMNP),[17] and 2-amino-5-nitropyridine (ANP).[17] These matrices provide a range of functional groups and acid/base characteristics. DHB, aTT, and dithranol are widely used matrices. DHB is a standard matrix used in the analysis of biomolecules in the reflectron mode and was chosen for this reason. Dithranol and aTT were chosen due to a desire to have matrices without strongly acidic and basic groups and due to their previous success as matrices with oligometallocenes[12a] and gangliosides,[16] respectively. AMNP and ANP have basic nitrogen groups and were chosen to provide a contrast with the acidic matrix DHB. Matrix solutions were made by dissolving 10 mg of the matrix in 1 mL of tetrahydrofuran or acetonitrile. Sample solutions were made fresh each day with a typical concentration being 1 mg/mL. Equal volumes of the solutions of the matrix and sample (typically 1 μL each) from the same solvent were mixed in a spot plate, and then a 0.5 μL sample of the mixture was deposited on the target. We also tried depositing the sample and matrix sequentially onto the target, but this was less successful because concentrated spots of the sample can result. Concentrated spots of sample negate the purpose of using a matrix, which is to isolate the analyte and to assist in desorption. The resulting spectra consist of the same fragments as seen without a matrix.

Spectra were calibrated internally and externally using C_{60} and C_{70} (720, 840 Da). When the mass peaks of interest exceeded 1900 Da, adrenocorticotropic hormone fragment [18-39] and bovine insulin were added and used in the calibration (2463.2, 5732.6 Da). When possible, spectra were also calibrated in the low mass range using matrix peaks. The m/z values determined experimentally agree within 0.03% of the calculated values except for several weak ion signals in the mass spectrum of $Cs_3Re_3Cl_{12}$ taken with matrices. These exceptions are noted within Table 1, which lists ions formed with matrices.

The most abundant peak of the isotope envelope is reported for all m/z values. Isotope patterns were calculated with Micromass (Manchester, UK) OPUS software. The isotope abundances of rhenium isotopes, ^{185}Re (37.07%) and ^{187}Re (62.93%), chlorine isotopes, ^{35}Cl (75.4%) and ^{37}Cl (24.6%), and bromine isotopes, ^{79}Br (50.57%) and ^{81}Br (49.43%), led to distinctive patterns based on the number of rhenium and halides atoms. Use of the reflectron mode was necessary to obtain isotopic resolution. Resolution of the most abundant peaks of the isotopic envelopes were between 1500 and 1800 (full-width at half-maximum). Isotope patterns are used in conjunction with the m/z values in the analysis of the mass spectra.

Chemicals. Rhenium(III) chloride was purchased from Pressure Chemical (Pittsburgh, PA). Rhenium(III) bromide was purchased from Cerac Inc. (Milwaukee, WI). All other reagents were purchased from Aldrich Chemical Company (Milwaukee, WI). Commercial reagents were used as received except for tetrabutylammonium octachlororodirhenate which was recrystallized from acetonitrile/ether. Nonacid solvents were dried using standard procedures. Hydrobromic acid was distilled from red phosphorus prior to use.

---

(11) For an overview, see: Vertes, A., Gijbels, R., Adams, F., Eds. *Laser Ionization Mass Analysis;* Wiley: New York, 1993; Vol. 124.

(12) (a) Hillenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. T. *Anal. Chem.* **1991**, *63,* 1193A. (b) Karas, M.; Bahr, U.; Giessmann, U. *Mass Spectrom. Rev.* **1991**, *10,* 335. (c) Cotter, R. J. *Anal. Chem.* **1992**, *64,* 1027A. (d) Chait, B. T.; Kent, S. B. H. *Science* **1992**, *257,* 1885.

(13) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Macromolecules* **1995**, *28,* 4562.

(14) Recent references include: (a) Juhasz, P.; Costello, C. E. *Rapid Commun. Mass Spectrom.* **1993**, *7,* 343. (b) Karas, M.; Ehring, H.; Nordhoff, E.; Stahl, B.; Strupat, K.; Hillenkamp, F.; Grehl, M.; Krebs, B. *Org. Mass Spectrom.* **1993**, *28,* 1476. (c) Woods, A. S.; Buchsbaum, J. C.; Worrall, T. A.; Berg, J. M.; Cotter, R. J. *Anal. Chem.* **1995**, *67,* 4462. (d) Vitalini, D.; Mineo, P.; Di Bella, S.; Fragalà, I.; Maravigna, P.; Scamporrino, E. *Macromolecules* **1996**, *29,* 4478. (e) Campardo, L.; Gobbo, M.; Rocchi, R.; Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chim. Acta* **1996**, *245,* 269. (f) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62,* 1274. (g) Dale, M.; Knochenmuss, R.; Zenobi, R. *Rapid Commun. Mass Spectrom.* **1997**, *11,* 136.

(15) Strupat, K.; Karas, M.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *111,* 89.

(16) Juhasz, P.; Costello, C. E. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 785.

(17) Fitzgerald, M. C.; Parr, G. R.; Smith, L. M. *Anal. Chem.* **1993**, *65,* 3204.

Table 1. Summary of Matrix Adduct Ions of $Cs_3Re_3Cl_{12}$ Detected Using a Variety of Matrices

	DHB[a]		aTT[a]		AMNP[a]		ANP[a]	
	calcd[b]	expt	calcd[b]	expt	calcd[b]	expt	calcd[b]	expt
$Re_3Cl_6(\text{matrix-H})^-$	923.69	924.6[d]						
$Re_3Cl_7(\text{matrix-H})^-$	958.66	958.6	947.65	946.9[d]				
$Re_3Cl_6(\text{matrix-H})_2{}^-$	1076.71	1076.6	1054.69	1054.8				
$Re_3Cl_8(\text{matrix-H})^-$	995.63	995.6	984.62	984.8	994.66	994.2[c]	980.64	979.4[d]
$Re_3Cl_7(\text{matrix-H})_2{}^-$	1111.68	1111.5	1091.66	1091.8	1109.73	1109.1[c]	1081.70	1081.4
$Re_3Cl_6(\text{matrix-H})_3{}^-$	1229.73	1229.0[c]	1196.70	1196.8				
$Re_3Cl_9(\text{matrix-H})^-$	1030.60	1030.6	1019.59	1019.9	1029.62	1029.1[c]	1015.61	1015.4
$Re_3Cl_8(\text{matrix-H})_2{}^-$	1148.65	1148.5	1126.62	1126.8	1146.70	1146.0[c]	1118.67	1118.3[c]
$Re_3Cl_7(\text{matrix-H})_3{}^-$	1264.70	1264.2[c]						
$Re_3Cl_9(\text{matrix-H})_2{}^-$			1161.59	1161.8				

[a] As with the studies without a matrix, oxygen containing ions were seen in varying abundances in different samples. [b] Calculated values are in daltons. [c] *m*/*z* experimental values agree within 0.06% of the calculated values. [d] *m*/*z* experimental values agree within 0.1% of the calculated values.

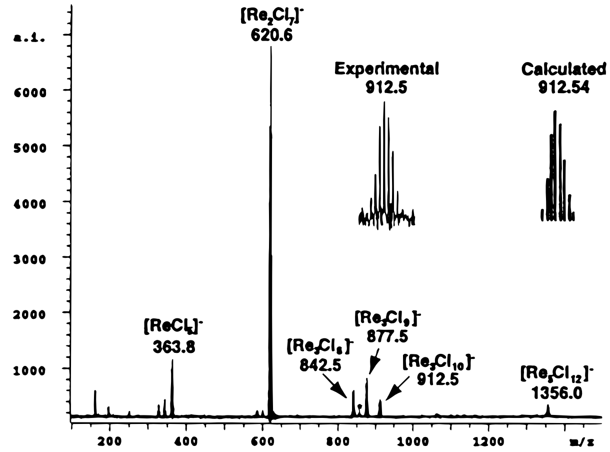


Figure 1. LDI mass spectrum of $Cs_3Re_3Cl_{12}$ (without any matrix) recorded in the negative ion mode.

$Cs_3Re_3Cl_{12}$,[2,18] $Cs_3Re_3Br_{12}$,[2] and $[Et_4N][Re_3Cl_{10}(H_2O)_2]\cdot 2H_2O$[19] were prepared by literature methods. Single maroon crystals of $Cs_3Re_3Cl_{12}$ were formed by dissolving the compound in hot concentrated aqueous HCl and cooling in the refrigerator. X-ray crystal structure analysis confirmed the crystal's identity. Recrystallization of $Cs_3Re_3Br_{12}$ from hot aqueous HBr gave black crystals.[20] $[Et_4N][Re_3Cl_{10}(H_2O)_2]\cdot 2H_2O$ crystallized from the reaction mixture as dark maroon crystals.

Results and Discussion

Negative mode MALDI and LDI mass spectra provide the most valuable information. Positive mode MALDI and LDI mass spectra taken at the threshold of ion formation/desorption did not contain peaks due to any rhenium containing species. The positive mode spectra did confirm the identity of the cation. Ion signals for each rhenium halide species give a distinctive envelope of peaks due to the isotopes and the isotopic abundances of rhenium and chlorine; for an example, see the insert in Figure 1. (In the discussion of spectra the term "ion signal" will be used to refer to the envelope of peaks resulting from an ion.) For singly charged ions, the individual peaks of the ion signal are two units apart due to the isotopes of rhenium (185, 187) and chlorine (35, 37). Spectra of rhenium bromide species have the same general features as those for rhenium chloride species. All of the species discussed in this paper desorb both with and without a matrix and the ionization step is not necessarily needed since they are all ionic. However, some of the detected ion signals have been attributed to ionized neutral fragments.

The negative ion LDI mass spectrum of $Cs_3Re_3Cl_{12}$ (without a matrix) is presented in Figure 1. The ion signals seen in the spectrum correspond to the following species: $[Re_5Cl_{12}]^-$ (expt 1356.0, calcd 1356.39 Da), $[Re_3Cl_{10}]^-$ (expt 912.5, calcd 912.54 Da), $[Re_3Cl_9]^-$ (expt 877.5, calcd 877.58 Da), $[Re_3Cl_8]^-$ (expt 842.5, calcd 842.61 Da), $[Re_2Cl_7]^-$ (expt 620.6, calcd 620.69 Da), and $[ReCl_5]^-$ (expt 363.8, calcd 363.80 Da). The isotope patterns in the experimental data match those calculated. The matching experimental and calculated isotope pattern for the ion signal for $[Re_3Cl_{10}]^-$ are shown in the insert of Figure 1.

The positive ion LDI mass spectrum of $Cs_3Re_3Cl_{12}$ (without a matrix) contains ion signals for $[Cs]^+$, $[Cs_2Cl]^+$, and $[Cs_3Cl_2]^+$, identifying the cation as cesium.

The laser power greatly influences the anions detected in the MS experiment. In the LDI experiment on $Cs_3Re_3Cl_{12}$ (without a matrix) an increase in the laser power to well over the threshold of ion formation/desorption results in the formation of aggregates up to *m*/*z* values of over 5000 representing species with one to twenty rhenium atoms. These ions are presumed to have been formed in the plume, which is the collection of ions and neutral molecules expelled into the gas phase from the solid sample when laser energy is absorbed. All of the ion signals discussed in reference to Figure 1 are very intense in spectra taken when the laser power is well above the threshold of ion formation/desorption. A representative LDI mass spectrum with high laser power is presented in Figure 2. All ions detected are singly charged species, on the basis the spacings (±2 units) within the peaks of the ion signal. The repeating sets of ion signals in the *m*/*z* range of 1700−5000 differ by one rhenium atom. These repeating sets display a difference in *m*/*z* ratio of 35, representative of a chlorine, within each set of ion signals corresponding to a given Re_n aggregate and the isotope pattern of each ion signal is characteristic of rhenium chloride species. The insert of Figure 2 shows a set of ion signals that contains twelve rhenium atoms and differs by one chlorine. The most abundant ion signal in that set can be attributed to $[(Re_3Cl_9)_n]^-$ ($n = 4$), which can be considered a portion of the polymer $(Re_3Cl_9)_n$.

The ion signal in LDI mass spectra at 1356.0, which is detected even when the laser power is at the threshold of ion formation/desorption (displayed in Figure 1), matches both the calculated *m*/*z* value and the isotope pattern for $[Re_5Cl_{12}]^-$. While the other ion signals in the LDI mass spectra when the laser power is at the threshold of ion formation/desorption were fragments of the parent anion, $[Re_3Cl_{12}]^{3-}$, this ion signal with

---

(18) Bertrand, J. A.; Cotton, F. A.; Dollase, W. A. *Inorg. Chem.* **1963**, *2*, 1166.

(19) Irmler, M.; Meyer, G. *Z. Anorg. Allg. Chem.* **1989**, *579*, 116.

(20) The crystal structure of $Cs_3Re_3Br_{12}$ has been reported: Elder, M.; Gainsford, G. J.; Papps, M. D.; Penfold, B. R. *J. Chem. Soc., Chem. Commun.* **1969**, 731.

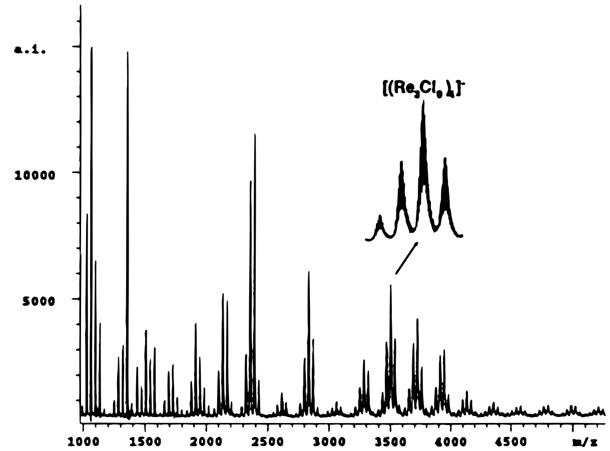


Figure 2. LDI mass spectrum of $Cs_3Re_3Cl_{12}$ (without any matrix) recorded in the negative ion mode with the laser power well above the threshold for ion formation/desorption.

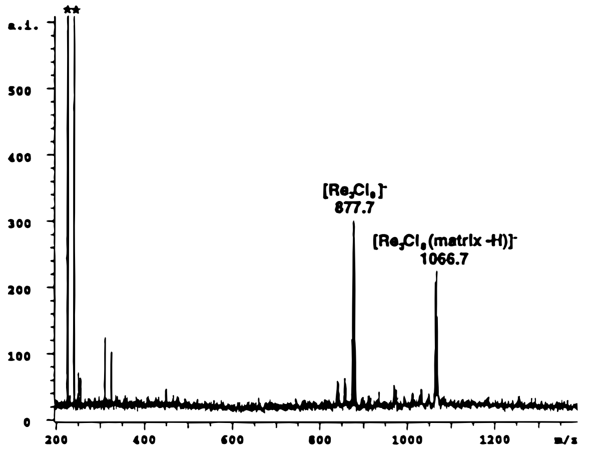


Figure 3. MALDI mass spectrum of $Cs_3Re_3Cl_{12}$ in the matrix dithranol recorded in the negative ion mode. Peaks marked with an asterisk are due to the matrix.

a nuclearity higher than the parent anion was unexpected. This species is most likely formed in a gas phase ion−molecule or ion−ion reaction in the plume. That this cluster forms even when the laser power is just above the threshold of ion formation is suggestive of the stability of this ion. Pentanuclear clusters of rhenium have not been reported in the literature,[1,21] but the detection of this cluster leads us to speculate that a stable pentanuclear cluster of rhenium might be anticipated.

The negative ion LDI mass spectrum of $Cs_3Re_3Br_{12}$ (without a matrix) has the same general features as the mass spectrum of $Cs_3Re_3Cl_{12}$ although the relative intensities between the ion signals were different and the best signal-to-noise ratio for the ion signals was lower. As a result, the ion signal for $[Re_3Br_{10}]^-$ was often too weak for an *m/z* value to be assigned definitively, but was present in the baseline. The most abundant peak corresponds to $[Re_2Br_7]^-$ (expt 932.5, calcd 932.33 Da); with $Cs_3Re_3Cl_{12}$ the most abundant peak was $[Re_2Cl_7]^-$ when spectra were collected without a matrix. There is also a series of peaks which are attributed to bromine loss, $[Re_3Br_9]^-$ (expt 1277.3, calcd 1277.12 Da) and $[Re_3Br_8]^-$ (expt 1198.5, calcd 1198.20 Da). The pentanuclear species $[Re_5Br_{12}]^-$ (expt 1889.7, calcd 1889.78 Da) is detected although with a very poor signal-to-noise ratio. The positive mode LDI mass spectrum reveals the cation as Cs^+.

LDI mass spectrometry has been used in the analysis of inorganic and organometallic complexes. The technique has been shown to cause aggregation in neutral complexes.[22] In other studies molecular ions have been detected, but many fragments were also observed.[23] The presence of fragments in the spectra can make the analysis of LDI mass spectra of unknown complexes difficult.

In a successful MALDI experiment, the absorption of the laser energy by the matrix allows for the desorption of large molecules without fragmentation. The matrix also isolates the analyte, decreasing the likelihood of aggregation of analyte molecules.[12a,c] Thus, the addition of a matrix should lead to reduced fragmentation and aggregation of the analyte in the MS experiment.

As anticipated, spectra recorded with a matrix in this study exhibit less fragmentation and aggregation than spectra recorded without a matrix. Ion signals of trinuclear species dominate the MALDI-TOF mass spectra of $Cs_3Re_3Cl_{12}$ in matrices. Dinuclear and mononuclear species seen in the spectra taken without a matrix are eliminated in all cases except for a very weak signal for a dinuclear species in the spectrum of $Cs_3Re_3Cl_{12}$ recorded with DHB as the matrix. Also, the ion signal for $[Re_5Cl_{12}]^-$ was not present upon the addition of a matrix, further evidence that this species is the product of a reaction in the plume.

All of the matrices investigated in this study give mass spectra containing ion signals for rhenium halide matrix adduct ions (referred to as matrix adduct ions in the text of this paper) along with trinuclear ions without adducted matrix. For singly charged matrix adduct ions, the most abundant peaks of the ion signal are two mass units apart. In addition, peaks of much less abundance at one mass unit apart are found between some of these peaks. These less abundant peaks are due to isotopes of elements (^{13}C, ^{2}H) in the matrix-derived portion of the ion.

Matrix adduct ions are thought to be formed in gas phase reactions from fragment ions or neutrals of the rhenium halide species and matrix-derived ions or neutrals. The literature on MALDI-TOF MS recognizes such reactions. Ion−molecule reactions between desorbed analyte molecules and matrix-derived ions or co-desorbed metal ions in the gas phase have been proposed for the cationization of peptides.[24,25] Matrix adduct ions have been previously reported for polymer analytes with divalent and trivalent metal ions as cationization reagents.[26] In that work quasimolecular ions of the type $[P + M + (\text{matrix-H})]^+$ or $[P + M + (\text{matrix-2H})]^+$ (where P is polyethylene oxide dimethyl ether and M is a di- or trivalent metal cation) were detected upon the addition of di- or trivalent metal ions.

Figure 3 presents the MALDI mass spectra of $Cs_3Re_3Cl_{12}$ in the matrix dithranol. Using this matrix resulted in the fewest ion signals for the $[Re_3Cl_{12}]^{3-}$ anion and gave very few matrix

---

(21) For a review of known cluster types and examples, see: Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840.

(22) (a) Dale, M. J.; Dyson, P. J.; Suman, P.; Zenobi, R. *Organometallics* **1997**, *16*, 197. (b) Dale, M. J.; Dyson, P. J.; Johnson, B. F. G.; Langridge-Smith, P. R. R.; Yates, H. T. *J. Chem. Soc., Dalton Trans.* **1996**, 771. (c) Dale, M. J.; Dyson, P. J.; Johnson, B. F. G.; Martin, C. M.; Langridge-Smith, P. R. R.; Zenobi, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1689.

(23) (a) Bjarnason, A. *Rapid Commun. Mass Spectrom.* **1989**, *3*, 373. (b) Bjarnason, A.; DesEnfants, R. E., II; Barr, M. E.; Dahl, L. F. *Organometallics* **1990**, *9*, 657. (c) Marchon, J.-C.; Wilkins, C. L.; Yang, L.-C. *Org. Mass Spectrom.* **1989**, *24*, 197. (d) Brown, R. S.; Wilkins, C. L. *Anal. Chem.* **1986**, *58*, 3196.

(24) Wang, B. H.; Dreisewerd, K.; Bahr, U.; Karas, M.; Hillenkamp, F. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 393.

(25) Ehring, H.; Karas, M.; Hillenkamp, F. *Org. Mass Spectrom.* **1992**, *27*, 472.

(26) Wong, C. K. L.; Chan, T.-W. D. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 513.

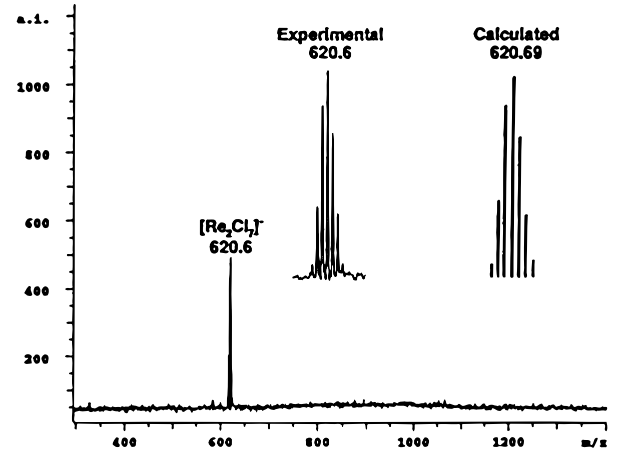


Figure 4. LDI mass spectrum of $[Bu_4N]_2Re_2Cl_8$ (without any matrix) recorded in the negative ion mode.

peaks. There are only two major ion signals due to rhenium containing species corresponding to $[Re_3Cl_9]^-$ (expt 877.7, calcd 877.58 Da) and $[Re_3Cl_8(\text{matrix-H})]^-$ (expt 1066.7, calcd 1066.66 Da). Table 1 shows the assignment of the resolved ion signals with the general composition $[Re_3Cl_x(\text{matrix-H})_y]^-$ ($x = 6-9$, $y = 1-3$) in the negative ion MALDI mass spectra of $Cs_3Re_3Cl_{12}$ using the four other matrices selected for this study, DHB,[15] aTT,[16] AMNP,[17] and ANP.[17] It is noteworthy that species bearing a −2 or −3 charge are not detected.

The matrices DHB, aTT, and dithranol give much better signal to noise for the adduct ion signals than the other two matrices. With the matrices DHB, aTT, AMNP, and ANP the ion signals from ions formed by gas phase ion/molecule reactions between desorbed analyte fragments and matrix-derived ions dominate the mass spectra. The spectra taken with these matrices are further complicated by overlapping isotope patterns due to the adduction of matrix-derived ions/molecules with varying numbers of hydrogen. Some matrix-derived ions/molecules have lost one or two hydrogens. This is a reasonable occurrence since the ions $[\text{matrix-H}]^-$ and $[\text{matrix-2H}]^{\bullet-}$, where the matrix is DHB, have been identified as ions formed in the ultraviolet laser ionization/desorption of DHB.[25]

One goal in the characterization of trinuclear rhenium(III) species is to establish the presence of three rhenium atoms in the species being analyzed. Since we have seen that aggregation of rhenium atoms and loss of nuclearity can occur in the LDI mass spectrometry experiment, it is important to establish conditions that suppress aggregation and loss of nuclearity. Recording the mass spectra in a matrix suppresses aggregation and loss of nuclearity, while, without a matrix, only aggregation is suppressed for spectra recorded at or just above the threshold of ionization/desorption. To test if this is a general observation for species with fewer rhenium atoms, the dinuclear $(Bu_4N)_2[Re_2Cl_8]$ was investigated. The greater solubility of this compound versus $Cs_3Re_3Cl_{12}$ in organic solvents also allowed for the investigation of the effect of concentration of the analyte.

The negative ion LDI mass spectrum of $(Bu_4N)_2[Re_2Cl_8]$ (without a matrix) is presented in Figure 4. Note that the only species detected is the fragment ion $[Re_2Cl_7]^-$ (expt 620.6, calcd 620.69 Da), where the dianion has lost one chloride ion becoming a monoanion. The insert in Figure 4 shows the experimental and calculated *m/z* values and isotope pattern for the ion $[Re_2Cl_7]^-$. The agreement between the experimental and calculated patterns confirms the assignment of this ion signal. Again multiply charged anions are not detected although the anion of the analyte has a −2 charge. The positive ion mass spectrum did not reveal any positively charged rhenium containing species, and only confirms that the cation is $[Bu_4N]^+$.

MALDI-TOF MS studies on $(Bu_4N)_2[Re_2C1_8]$ in DHB with varying analyte/matrix ratio showed that concentration of the analyte in the matrix had a minimal effect on the mass spectra. The major ions detected were the same over the range of 1800 to 22 pmol deposited on the target with 34 000 pmol of matrix. The resolved rhenium-containing ion signals were attributed to the following anions: $[Re_2Cl_7]^-$ (expt 620.8, calcd 620.69 Da), $[Re_2Cl_6(\text{DHB-H})]^-$ (expt 738.8, calcd 738.74 Da), and $[Re_2Cl_5(\text{DHB-H})_2]^-$ (expt 854.9, calcd 854.79 Da). However, at the lower concentrations matrix adduct ions of the type $[Re_2Cl_x(\text{DHB-H})_y]^-$ ($x = 4$, $y = 2-3$ and $x = 5$, $y = 1$) were present in the baseline. The signal to noise ratio was better at higher concentrations of the sample.

In most negative mode LDI mass spectra taken of $Cs_3Re_3Cl_{12}$ (without a matrix), a peak at 858.6 Da is detected (a weak ion signal marked with an asterisk in Figure 1). This peak was identified as $[Re_3Cl_8O]^-$, on the basis of its *m/z* value and isotopic pattern. In spectra taken with matrices, adduct peaks for the ions $[Re_3Cl_xO(\text{matrix-H})_y]^-$ ($x = 6-8$, $y = 1-2$) are detected. The intensity of these oxygen containing peaks varied among the samples used. The best spectra, those in which the oxygen containing peaks were the least intense, arose with noncrystalline (powder) samples which had been dried carefully. No oxygen-containing peaks were detected in the spectra of $[Bu_4N]_2[Re_2Cl_8]$.

The origin of oxygen-containing ion signals in these various spectra was a concern because oxygen is not formally part of the compound. Of several possibilities, we favor an explanation which assumes the presence of small amounts of water in the crystalline lattice. The traditional preparation and purification of $Cs_3Re_3Cl_{12}$ involves an aqueous acid medium. Analytical techniques used (elemental analysis and X-ray crystallography) to identify this as an anhydrous species would probably not have picked up residual water. The presence of water, even in small amounts, in the ion−molecule mix within the plume in the MALDI experiment would likely present an ideal opportunity to incorporate oxygen into an anion.

Other possible explanations for the presence of oxygen in the sample would place small amounts of water or hydroxide ion in the metal coordination sphere of rhenium. The competition between water and chloride ion to occupy an equatorial coordination site on the trirhenium cluster anion has been recognized,[27] and several trirhenium cluster complexes in which water and chloride occupy equatorial coordination sites are known.[19,28] Water or hydroxide, in small amount and possibly distributed in several sites in the molecule, would not likely have been detected in the previous characterization of these species.

Regardless of the origin of oxygen, however, the presence of this element can have significant consequences. In recent work, we showed that when these rhenium(III) cluster compounds dissolved in acetonitrile, acetamidate complexes are formed.[29] The acetamidate ligand arises from addition of water to the solvent. Considering this, a procedure that identifies the

---

(27) Irmler, M.; Meyer, G. *Naturwissenschaften* **1987**, *74*, 492.

(28) (a) Jung, B.; Meyer, G.; Herdtweck, E. A. *Z. Anorg. Allg. Chem.* **1991**, *604*, 27. (b) Irmler, M.; Meyer, G. *J. Less-Common Metals* **1987**, *132*, 133. (c) Meyer, G.; Irmler, M. *Z. Anorg. Allg. Chem.* **1986**, *534*, 115. (d) Elder, M.; Gainsford, G. J.; Papps, M. D.; Penfold, B. R. *J. Chem. Soc., Chem. Commun.* **1969**, 731. (e) Penfold, B. R.; Robinson, W. T. *Inorg. Chem.* **1966**, *5*, 1758.

(29) McGaff, R. W.; Dopke, N. C.; Hayashi, R. K.; Powell, D. R.; Treichel, P. M. Unpublished results.

presence of small amounts of water in a sample of metal cluster could be potentially useful.

We synthesized the known compound $[Et_4N][Re_3Cl_{10}(H_2O)_2]\cdot 2H_2O$[19] to further evaluate the effect water had on the spectra. In the negative ion LDI mass spectrum of this compound (without a matrix) the fragment $[Re_3Cl_8O]^-$ (expt 858.7, calcd 858.6 Da) is the most abundant peak in the spectrum. When the mass spectrum is recorded with the matrix dithranol the most abundant peak is $[Re_3Cl_9]^-$ (expt 877.8, calcd 877.58 Da). The other trinuclear fragments, such as $[Re_3Cl_8O]^-$, are much less abundant in comparison to the $[Re_3Cl_9]^-$ signal. As with $Cs_3Re_3Cl_{12}$ none of the smaller fragments, $[Re_2Cl_7]^-$ and $[ReCl_5]^-$, is present in the spectra with dithranol.

The abundance of the ion signal for $[Re_3Cl_9]^-$ noted in the spectra recorded in dithranol for $Cs_3Re_3Cl_{12}$ and $[Et_4N][Re_3Cl_{10}(H_2O)_2]\cdot 2H_2O$ is not surprising considering the radiochlorine exchange experiments on the anion $[Re_3Cl_{12}]^{3-}$ completed by Robinson and Fergusson.[2] These experiments showed that exchange is rapid for the three in-plane terminal ligands. Thus, it is logical that the most abundant rhenium containing ion signal in the mass spectra with dithranol be a cluster that shows the composition of the core, the species after losing the three in-plane terminal ligands. In both of the trinuclear species investigated the core cluster is Re_3Cl_9.

At no point during our studies was a multiply charged anion detected. Equally interesting is that no cation−anion pairs, such as $[Cs_2Re_3Cl_{12}]^-$ or $[CsRe_3Cl_{11}]^-$, are detected in the negative mode although one might have predicted these ions would have been formed. Cation/anion pairs of the form $[C_{n+1}A_n]^+$ and $[C_nA_{n+1}]^-$ generally form for monovalent cations and anions when analyzed by laser desorption mass spectrometry.[30] Cation/anion pairs have also been detected in electrospray experiments.[10] One explanation for the lack of cation−anion pairs is that the loss of chloride ions from the cluster to cesium ions during desorption or in the gaseous cloud (plume) just above the target immediately following the laser pulse is a very favorable process. The pairing of cesium cations and chlorine anions seen in the positive mode mass spectra substantiates this analysis. We speculate that the kinetic lability of the chloride ligand contributes to the preference for the loss of chloride ions from the multiply charged parent ion to form singly charged anionic species.

Conclusion

Although MALDI-TOF MS is a widely used technique in the areas of polymer and biochemistry, this technique has not yet received much attention in the inorganic chemistry community. A primary goal of this research project was to establish MALDI-TOF MS as a useful characterization tool in this area, specifically in the chemistry of metal atom clusters. Because it is a relatively easy experimental procedure, a soft ionization technique, and applicable to a wide range of compounds including ionic species, the addition of MALDI-TOF MS to the arsenal of techniques available to inorganic chemistry would be a worthwhile achievement. The results we have assembled on the MALDI mass spectra of several classic rhenium(III) cluster species suggest a qualified success in achieving this overlying goal.

In this work, conditions were determined that provided useful, reproducible spectra for $Cs_3Re_3X_{12}$ ($X = Cl, Br$), $(Et_4N)_2[Re_2Cl_8]$, and $[Et_4N][Re_3Cl_{10}(H_2O)_2]$. In all experiments, only ions with a -1 charge were seen, their formation apparently due to the facile loss of one or more halide ions or water molecules from the parent anion. This process apparently takes precedent over other processes such as the aggregation of cations and anions, a general process that commonly occurs in other systems. Establishing the preference for this type of reaction (the facile loss of a negative ion to reduce the overall charge) in negative ion MALDI-TOF MS is important since it precludes obtaining spectra of parent ions with charges greater than -1.

The negative mode MALDI-TOF mass spectra of the studied rhenium(III) halide species gave characteristic fragments which could be used to identify the number of rhenium atoms in the cluster. The observed ion signals in spectra taken with a matrix for the three trinuclear complexes in this study were identified as species having three metal atoms, while for the dinuclear species, the ion signals corresponded to dirhenium species. Matrices also suppressed aggregation to higher nuclearity species. Dithranol was the matrix found to give the least complicated, yet informative, mass spectra for $Cs_3Re_3Cl_{12}$.

It will be desirable to test the hypotheses offered here with other metal cluster species, to see if the observations can be further generalized. In addition, the area of positive ion MALDI-TOF MS to study metal cluster species remains open for study. Using $Cs_3Re_3Cl_{12}$ and $(Et_4N)_2[Re_2Cl_8]$ as principles in this study dictated that negative ion mass spectroscopy would receive principal attention. Other types of complexes prone to formation of positive ions will be needed in order to extend the usefulness of this technique in this direction. Hopefully, the results here, which are clearly informative on the specific systems used in this study, will encourage others to seek to apply this technique in other arenas of inorganic chemistry.

Acknowledgment. We thank Research Corporation and the University of Wisconsin−Madison Graduate School for the grant to support part of this research. National Science Foundation Award No. 9520868 was used to purchase the Bruker REFLEX II Mass Spectrometer. We also thank Dr. Douglas R. Powell for the X-ray crystallography data collection and structure solution.

IC971220P

---

(30) Hercules, D. M.; Day, R. J.; Balasanmugam, K.; Dang, T. A.; Li, C. P. *Anal. Chem.* **1982**, *54*, 280A.