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Characterization of $\{M_8[S_2CC(CN)_2]_6\}^{4-}$, where $M = Cu^I$ and Ag^I, homocubane clusters by ^{252}Cf-plasma desorption mass spectrometry

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Dedicated to the recognition of the many contributions to mass spectrometry of Jesse (Jack) Beauchamp on his 60th birthday.

Abstract

The molecular weights of homocubane clusters, $[M_8L_6]^{4-}$ where $M = Cu^I$ and Ag^I, containing 1,1-dicyano-ethylene-2,2-dithiolate ligands have been determined by ^{252}Cf-plasma desorption mass spectrometry. In addition to the expected parent ion, an unexpected pentaanionic cluster also was observed for both metal systems. These studies affirm the versatility of ^{252}Cf-PDMS for providing a rapid verification of the purity and formulation of high nuclearity cluster compounds. (Int J Mass Spectrom 222 (2003) 493–501)

Keywords: Homocubane clusters; Plasma desorption mass spectrometry; Pentaanionic clusters

1. Introduction

The synthesis and characterization of large metal cluster compounds is of fundamental interest because their unique chemical and physical properties are intermediate between the atomic and bulk properties of a metal [1]. As a result, these types of clusters can, for example, be used to study the reactions that occur on the surface of highly dispersed metal particles used in heterogeneous catalysis [2]. The structural characterization of large metal clusters is often problematic because of difficulties in producing crystals amenable to X-ray diffraction (XRD) or the inability to distinguish similar clusters by conventional spectroscopic methods. In principle, mass spectrometry should be able to provide rapid information concerning the purity, formulation and possibly the bonding arrangement of these clusters. Nearly a decade ago, we began to investigate the application of ^{252}Cf-plasma desorption mass spectrometry (PDMS) as a means of characterizing a variety of metal clusters. We reported the results for a wide variety of complexes including a large gold cluster (Au_{55}) [3], and various close-packed and triangular platinum carbonyl complexes including $[Pt_9(CO)_{18}]^{2-}$, $[Pt_{19}(CO)_{22}]^{4-}$, $[Pt_{26}(CO)_{32}]^{2-}$ and $[Pt_{38}(CO)_{44}]^{2-}$ [4]. In all of

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these cases, ^{252}Cf-PDMS provided a rapid assay of the sample composition of these complexes in lieu of or in advance of a more definitive structural characterization by XRD. Over the intervening decade, this mass spectrometric method along with other approaches including fast atom bombardment-MS (FAB-MS) and secondary ion-MS (SI-MS), both of which had also been used to study smaller metal clusters [5], have largely been supplanted by matrix assisted laser desorption-MS (MALDI) and electrospray ionization-MS (ESI-MS). These MS methods, both commercially available, have been successfully used in a wide variety of applications including the structural analyses of large inorganic complexes. Johnson has recently described a comparison of both of these methods to study large osmium clusters citing many of the recent articles that describe the use of these methods to a variety of metal cluster complexes [6]. There are however, very few reports of the analysis of any type of copper- or silver-chalcogenide clusters by mass spectrometry except for the results described by Dance and coworkers utilizing laser ablation combined with FT-ICR mass spectrometry to examine a series of metal-chalcogenide cluster ions [7].

In this report, we describe the results obtained for tetra-*n*-butyl ammonium salts of cubic octanuclear Cu^I and Ag^I clusters containing *i*-MNT, $[S_2CC(CN)_2]^{2-}$, ligands, L. We were able to confirm the molecular weight of the intact $[(n\text{-}Bu_4N)_4M_8L_6]$ complex from the positive ion ^{252}Cf-PD mass spectrum. In addition to the tetraanionic complex, $[M_8L_6]^{4-}$, with its four charge balancing $(n\text{-}Bu_4N)^+$ cations an additional peak corresponding to a pentaanionic species, $[M_8L_6]^{5-}$, was detected. The negative ion spectrum contained peaks in the low mass range that were associated with the ligand and an unusual polymeric pattern of peaks extending beyond *m*/*z* 2000. Determination of the formulation and structure of metal clusters such as these is often hindered by difficulties in preparing crystals suitable for XRD studies, especially as the synthetic protocols are being refined. This study adds to the growing list of metal cluster compounds amenable to analysis by MS and in general, confirms the versatility and utility of this approach to rapidly identify and screen the products of a cluster synthesis often, in advance of more detailed structural studies by other spectroscopic methods.

2. Experimental

The syntheses of $[(n\text{-}Bu_4N)_4Cu_8(i\text{-}MNT)_6]$ (**1**), and $[(n\text{-}Bu_4N)_4Ag_8(i\text{-}MNT)_6]$ (**2**), followed the procedures previously reported [8]. Both compounds were characterized by IR, ^{13}C-NMR and single crystal cell-constant check, and found identical to those reported. $[(n\text{-}Bu_4N)_4Cu_8(i\text{-}MNT)_6]$ was dissolved in acetone and $[(n\text{-}Bu_4N)_4Ag_8(i\text{-}MNT)_6]$ was dissolved in CH_2Cl_2. The solution concentrations were 10^{-3} M. The sample backing consisted of a 1.5 μm aluminized Mylar foil (Atlan-Tol) that had been sputter-coated with 50 nm of Au (Hummer-X, Technics) on the metallized side to prevent aluminum oxide peaks from appearing in the mass spectrum. The complex was electrosprayed [9] directly onto the Au/Al Mylar that was coated with Hybond N+ (Amersham). The use of selected ion-polymer backings such as the Hybond have been found to facilitate the desorption–ionization of these types of metal cluster compounds. Minimal, if any spectrometric data has been obtained without the incorporation of surfaces of this type [10]. The Hybond N+ surface was prepared by dissolving 10 mg of the membrane in 1 mL of formic acid. After several hours, an insoluble part of the membrane still remained; the concentration of the final solution was 2 mg/mL. Approximately 50–100 μL, 10^{-3} M solution was adsorbed for 3 min; excess solution was removed by spinning the film at 10,000 rpm.

A description of the ^{252}Cf-PD mass spectrometer (constructed at Texas A&M), and associated electronics and data analysis system has been previously described [11]. This instrument was commercially marketed by Applied Biosystems, Inc. (BioIon 10 system). The ^{252}Cf fission fragment flux was ca. 1000 s^{-1}. The length of the time-of-flight (TOF) mass analyzer was 32 cm. The acceleration voltage was +12 and −10 kV. Useful data was obtained after a 30 min data acquisition; however, to obtain statistically better masses for the low intensity ions, data for some samples were acquired overnight (10 h). The mass calibration was obtained using the peaks in the mass spectrum due to H^+ and Na^+ for the positive ion spectrum and H^- and C_2H^- for the negative ion spectrum. The calibration is carried out in the following manner. The time digitizer measures the TOF for each ion to ±78 ps. A preliminary run is made to determine the TOF of the calibration ions to ±1 ns. The data acquisition software is programmed to identify those ions that have a TOF within ±10 ns of the TOF of the calibration ions as the ions to be used for the mass calibration. This data is stored in a separate location in the computer. The TOF of ions that are not in the calibration ion window are truncated to ±1.25 ns and are stored in another file in the computer. At the end of the experiment, the calibration curve is generated from the TOF distribution of the calibration ions. Since the TOF measurement is digital and not analog, the calibration curve (TOF vs. $\sqrt{m/z}$) is linear. Using this scheme, the slope and y-intercept have a precision of 10^{-4}%. To determine the m/z of an unknown peak in the mass spectrum, the centroid of the TOF peak is determined and converted to m/z using the calibration equation. The entire procedure for obtaining m/z data from a run is automated. After the run is completed, the data are analyzed and converted into a table of m/z and intensity values and plots of the data are obtained. Fig. 2 is an example of the format where the data are plotted in 8 ns wide intervals. In cases where a closer inspection of a particular region is required, the selected region can be displayed using a narrow time bin. Fig. 3 shows the same data but displayed in 4 ns wide time bins. Note that the intensity scale is reduced by the same factor.

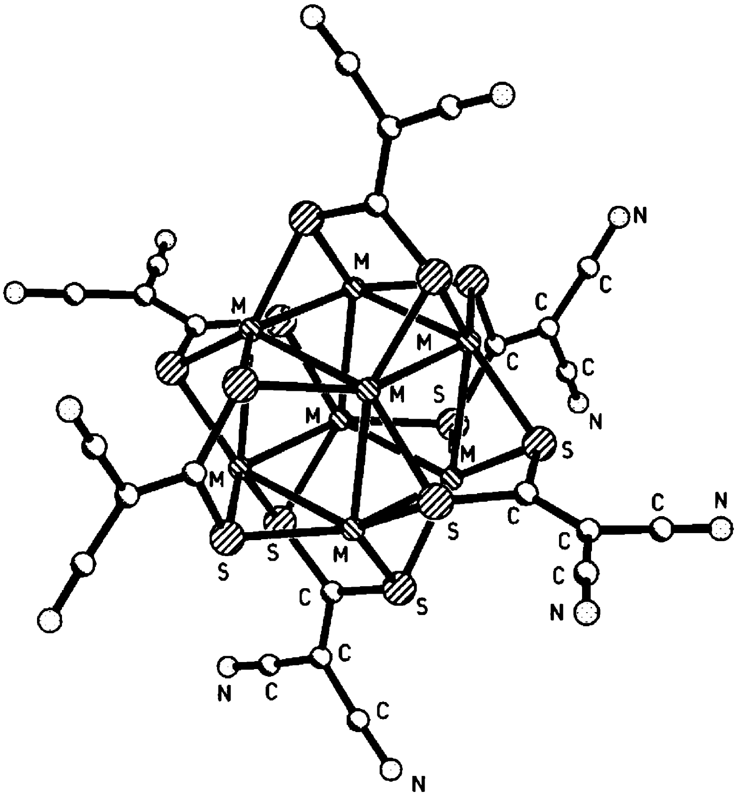

Fig. 1. The structure of $\{M_8[S_2CC(CN)_2]_6\}^{4-}$, where M = Cu^I and Ag^I, cluster anion.

3. Results

The structure of the titled homocubane cluster (Fig. 1) is represented as a slightly distorted cubical skeleton of eight metal atoms, each metal atom being bonded to three sulfur atoms of the different *i*-MNT ligands. Each face of the cube is further ligated by a tetradentate-CS_2 moiety of the ligand. This cluster has an idealized T_h point group symmetry [8]. The positive ion ^{252}Cf-PD mass spectrum of $[(n\text{-}Bu_4N)_4Cu_8(i\text{-MNT})_6]$ adsorbed on Hybond N+ is shown in Fig. 2; an expansion of the molecular ion region is shown in Fig. 3. Two principal peaks are observed in the high mass range at *m*/*z* 2569 and 2812. The structure of the *m*/*z* 2569 peak corresponds to the intact complex containing an additional *n*-butyl ammonium ion to form the adduct ion, $[(n\text{-}Bu_4N)_5Cu_8(i\text{-MNT})_6]^+$($M_{\mathrm{calc}} = 2562$). The mass of the second peak is 243 mass units higher than that of the adduct ion. This mass difference coincides closely with the mass of the $n\text{-}Bu_4N^+$ ion (242 u) and we propose that the structure of the second peak likely corresponds to a more reduced copper cubane cluster having a charge of −5 or results from the addition of a hydride ion to the tetravalent anion. Thus, the formula of this ion should correspond to $[(n\text{-}Bu_4N)_6Cu_8(i\text{-MNT})_6]^+$ ($M_{\mathrm{calc}} = 2804$) *or* $[(n\text{-}Bu_4N)_6Cu_8(i\text{-MNT})_6H]^+$ ($M_{\mathrm{calc}} = 2805$).

Although the peak width is not easily appreciated by examination of the single spectrum shown in Fig. 2, the species within this mass window were much broader than either other metal ion clusters (e.g., platinum carbonyl clusters) or biomolecules of similar *m*/*z*. When the mass spectrum is expanded (Fig. 3), it can be seen there is a high mass shoulder that is responsible for this broadening of each copper cubane ion peak. Each shoulder appears to consist of a set of barely resolvable component peaks, which seem to be separated by 5–7 u. The presence of these higher mass ions, incompletely resolved from the expected parent ion species, causes the calculated masses of these ions to differ from the expected calculated chemically averaged masses. (Chemically averaged masses are used because the individual isotopic contributions are generally not resolvable using the current instrumental resolution.) The composition of these components is still speculative, but we assume that they likely represent some type of adduct ion that may involve part of the Bu_4N^+ ion or gas phase rearrangements/adducts of the ligand [12].

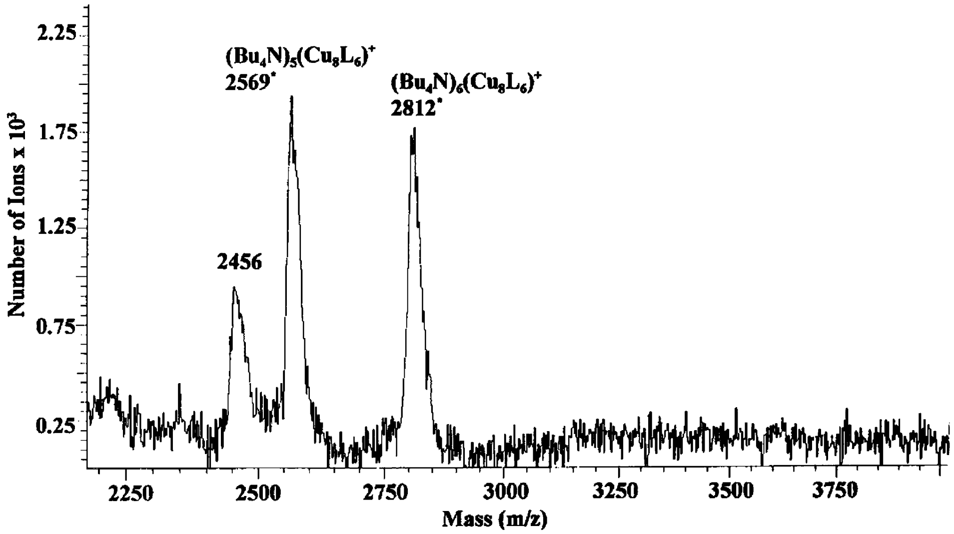

Fig. 2. The positive ion ^{252}Cf-PD mass spectrum of $[(n\text{-}Bu_4N)_4Cu_8(i\text{-MNT})_6]$ adsorbed on Hybond N+.

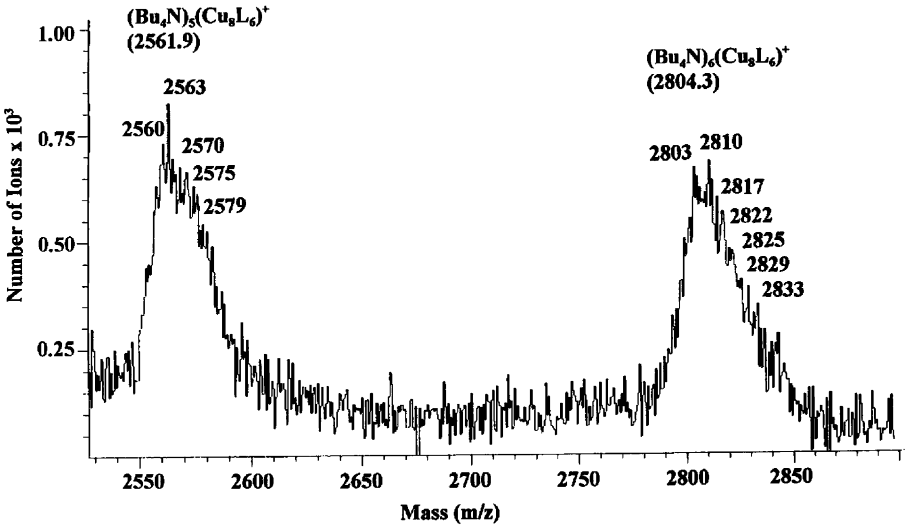

Fig. 3. The expansion of the molecular ion region of $[(n\text{-Bu}_4\text{N})_4\text{Cu}_8(i\text{-MNT})_6]$.

Very few fragment ion peaks are observed in the copper cubane positive ion spectrum. The peaks at *m/z* 2456 are attributed to either loss of CuSC ($M_{\text{calc}} = 2454$) or loss of $\text{SC}_2(\text{CN})_2$ ($M_{\text{calc}} = 2454$). In addition to this peak, ions are observed in low abundance at *m/z* 1022, 604, 401 and 312. The identities of these peaks have not been determined, but they do not seem to correspond to any structurally significant fragment ions. Abundant ions are detected of the $n\text{-Bu}_4\text{N}^+$ cation and many fragment ion peaks are observed for this species in the lower mass range (although none that could easily be associated with the parent ion adducts) [13].

The ^{252}Cf-PD negative ion spectrum of the copper cubane complex did not contain any peaks that could be correlated with the structure of the intact metal framework. Instead, two periodic patterns of peaks of equivalent and gradually diminishing intensities were observed extending from *m/z* 500 to beyond *m/z* 2000 (not shown). Each peak in both sets is separated by 159 u from the other members. The second set of peaks is shifted to a higher mass by ca. 66 u. One set of peaks has been identified as a copper sulfide polymer, $(\text{Cu}_2\text{S})_x{}^\bullet\text{HS}^-$ where values of x range from 3 to at least 12. The second pattern of peaks must also be a copper sulfide polymer since the mass difference between each member peak is the same as the first series. The 66 mass unit difference between the two series must be accounted for by the nature of the associated anion. One plausible structure that satisfies the observed mass shift corresponds to $(\text{Cu}_2\text{S})_x{}^\bullet\text{H}_2\text{S}_2{}^\bullet\text{HS}^-$.

The positive ion ^{252}Cf-PD mass spectrum of $[(n\text{-Bu}_4\text{N})_4\text{Ag}_8(i\text{-MNT})_6]$ adsorbed on Hybond N+ is shown in Fig. 4. Generally speaking, the pattern of the mass spectrum of the silver homocubane is similar to that of the copper homocubane shown in Fig. 2. The principal peak at *m/z* 2923 corresponds to the intact complex containing an additional *n*-butyl ammonium ion to form the adduct ion, $[(n\text{-Bu}_4\text{N})_5\text{Ag}_8(i\text{-MNT})_6]^+$ ($M_{\text{calc}} = 2916.4$). The peak at *m/z* 3160 can be formulated as $[(n\text{-Bu}_4\text{N})_6\text{Ag}_8(i\text{-MNT})_6]^+$ ($M_{\text{calc}} = 3158.8$), a homocubane cluster with a charge of -5 or, as described for the Cu cluster, a possible complex containing a hydride ion whose additional negative charge is balanced by the incorporation of the extra cation. Interestingly, a peak at *m/z* 5595 is also observed. It can be formulated as $\{[(n\text{-Bu}_4\text{N})_9][\text{Ag}_8(i\text{-MNT})_6]_2\}^+$ ($M_{\text{calc}} = 5589.8$). It is thought that this entity is a gas phase cluster rather than an impurity since there was no evidence

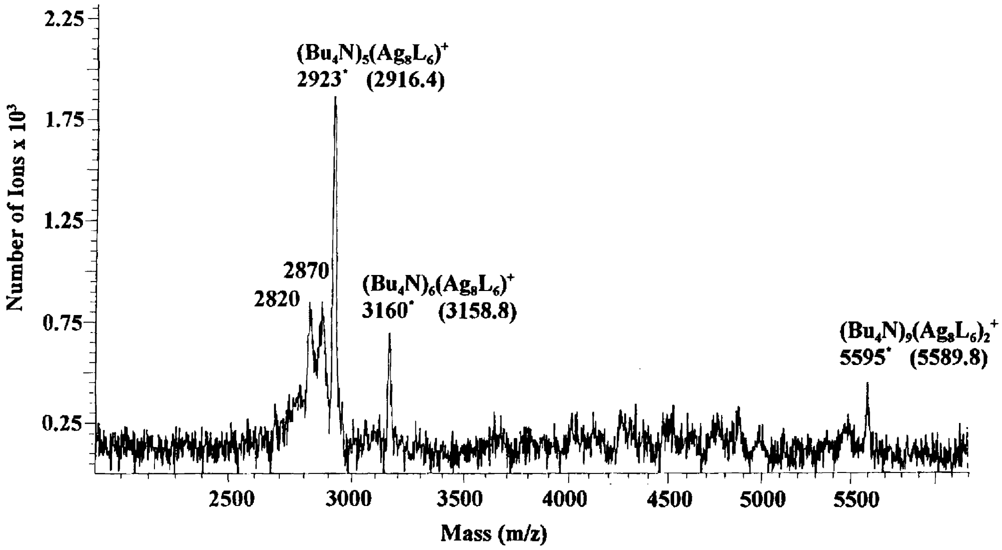

Fig. 4. The positive ion ^{252}Cf-PD mass spectrum of [(n-$Bu_4N)_4Ag_8$(i-MNT$)_6$] adsorbed on Hybond N+.

for its presence by other spectroscopic methods (see Section 4). As with the Cu cluster, very few fragment ion peaks are observed in the silver cubane positive ion spectrum. The peaks at m/z 2870 and 2820 are attributed to the loss of two and four CN groups, respectively ($M_{\mathrm{calc}} = 2864.4, 2812.4$). Comparing the calculated isotopic molecular weights of $[(n\text{-}Bu_4N)_5Ag_8L_6]^+$ and $[(n\text{-}Bu_4N)_6Ag_8L_6]^+$ with the two peaks in the spectrum, we find that the low mass edge of the peaks fit the calculation fairly well but the high mass edges are broadened. As with the Cu clusters, these peaks appear to contain adducts that produce a 'shoulder' on the high mass side (these are less apparent than in Fig. 2 since the mass range has been compressed). As with the copper cluster, the precise identity of these adducts is still unknown.

4. Discussion

The incorporation of the associated cation, n-Bu_4N^+ ion, to form a singly charged positive ion of complexes **1** and **2** is a process that has been previously reported in the positive ion FAB mass spectrum of $[(Et_4N)_2Fe_4S_4Br_4]$ [5d]. In fact, the addition of a cation to form the positive ion is the type of process commonly observed with salts of polyanionic biopolymers such as nucleic acids or polysulfated sugars. These salts form positive ions by the addition of one or more cations (usually Na^+ or K^+) than the number of negatively charged groups [14]. This desorption–ionization process therefore provides a convenient verification of the number of negatively charged functional groups on these polymers and, in the case of these metal clusters, identifies the composite charge of the metal cluster anion. In contrast to the anionic copper cluster, singly charged positive (and negative) ions of the di- and tetra-anionic platinum carbonyl clusters are formed primarily by electron loss. No incorporation of the associated cation (typically $[(Ph_3PCH_2C_5H_4)Fe(C_5H_5)]^+$), was observed even though the associated cation and its fragment ions were observed in high abundance in the positive ion spectra of these complexes. This undoubtedly relates to many inherent differences in the overall structure of these two types of metal–ligand complexes (e.g., Cu/Ag vs. Pt) including the electronic properties of the metal core as well as the character and binding of the associated ligands, especially as it relates to their relative nucleophilicities.

The observation that the molecular ion peak is actually a distribution of ions is a general phenomenon observed in the ^{252}Cf-PDMS data of many high nuclearity metal cluster compounds. Parent ions of the gold triphenylphosphine clusters and the platinum carbonyl complexes also exhibit a broadening of the parent ion peaks [3]. In the case of the larger gold clusters, e.g., Au_{55}, we were unable to resolve the components of the peak envelope and therefore could not conclusively identify the components. However, the ^{252}Cf-PDMS data we have obtained for small gold-triphenylphosphine clusters suggests that these distributions can, at least in part, result from a rapid shedding of gold atoms and ligands from the intact cluster whose mass might therefore best be represented by the high mass edge of this convolution of peaks [3b] in contrast to these Cu/Ag clusters where the parent ion mass more closely approximates the *low mass edge* of the distribution (as a result of adduct ions on the high mass edge). The individual components of the platinum carbonyl parent ion distributions were often resolvable and corresponded only to shedding of the carbonyl ligands; little or no disruption of the metal core was observed nor was any ligand rearrangement observed. Thus, it appears that the presence of multiple components in the parent ion peaks is often observed for high nuclearity clusters. However, the types of ions present in the peak envelope significantly differ depending on the identities of the metal atoms and ligands.

The reason for the discrepancy in the ratio of actual peak width to calculated isotopic peak width between Ag and Cu homocubanes is probably due to a combination of factors including the inaccuracy in the calculated masses due to the unresolved adduct ions. In addition some of the widening (and therefore the mass inaccuracy) may be due to the different internal energies of the ions. The heavier Ag ions are probably lower in energy and cooler than the Cu ions. The appearance of the plausible dimer adduct ion, $\{[(n\text{-}Bu_4N)_9][Ag_8(i\text{-MNT})_6]_2\}^+$, and the lack of its Cu compound counterpart is consistent with this assumption since cooling effects clustering [15]. Evidence for the pentaanionic cluster anion in the positive ion mass spectrum was unexpected. The question that arises is whether this species is present in solution or is formed during the desorption–ionization process. No change in cluster charge is observed in the ^{252}Cf-PDMS spectra of di- and tetra-anionic platinum carbonyl complexes [11]. Ideally this species can be formulated as either a reduced homocubane, $M_8L_6{}^{5-}$, or a cluster consisting of a hydride, $M_8L_6H^{5-}$. A hydride peak was not detected in the solution NMR of the crystalline starting materials. Cyclic voltammetry shows an irreversible peak at −1.35 V vs. Ag/AgCl [14]. This indicates that the electrochemically reduced homocubane does not survive in solution. Hence, we hypothesize that this intriguing species must be formed during the desorption–ionization process. In fact, the positive ion ^{252}Cf-PD mass spectrum of $[n\text{-}Bu_4N]_4[Cu_8(S_2CC(CN)(CO_2Et))_6]$ has also been determined. A peak at *m*/*z* 2847 in the positive ion spectrum is seen that corresponds to the homocubane with an additional *n*-butyl ammonium ion ($M^+_{\text{calc}} = 2841$). A second higher molecular weight ion was also observed at *m*/*z* 3085 peak that can be represented as $\{[n\text{-}Bu_4N]_6[Cu_8(S_2CC(CN)(CO_2Et))_6]\}^+$ ($M^+_{\text{calc}} = 3083$), a homocubane cluster with a charge of −5. This suggests that the peak whose mass corresponds to the intact molecular ion with two additional $n\text{-}Bu_4N^+$ ions appears to be general for Cu^I and Ag^I homocubane clusters.

What is the possible structure of the pentaanionic cluster anion? Both symmetry arguments and molecular orbital calculations [16] on the Cu_8S_{12} cluster suggest that the lowest energy empty atomic orbitals on each trigonally coordinated Cu^I atom combine to form low-lying a_{1g} and t_{1u} orbitals which become the LUMOs of this system. Thus, it is not surprising that these MOs can be filled with two or eight valence electrons in $Cu_8S_{12}X$ centered clusters, where $X = H^-$, Cl^-, Br^-, or S^{2-}. Indeed, centered-cubic clusters have been isolated and structurally characterized: $\{Cu_8[S_2P(O^iPr)_2]_6S\}$ [17a]; $\{Cu_8[S_2P(O^iPr)_2]_6Cl\}^+$ [17b,17c]; and $\{Cu_8[S_2P(O^iPr)_2]_6Br\}^+$ [17b]. Hence, the species $M_8L_6{}^{5-}$ can be tentatively assigned as $M_8L_6H^{5-}$ with a hydride, H^-, encapsulated in the center of the Cu_8 cubane (which has a cavity diameter of ca. 2.0 Å). At this time, a synthetic approach to this species is not yet available. The absence of any structurally significant fragmentation pattern in the positive ion mass spectrum is surprising since Coucouvanis has shown that the $[Cu_8(SL)_6]^{4-}$, L $=$ ^{t}Bu-DED, copper cubane cluster containing sulfur-rich dithiolate ligands reversibly dissociates into two $[Cu_4(SL)_3]^{2-}$ units in the presence of Na^+ or K^+ [18]. Indeed the $M_4L_4{}^{4-}$ tetrahedron has been structurally characterized with the *i*-MNT ligand, but its ^{t}Bu-DED counterpart has not been reported. If the smaller cluster, $[Cu_4(i\text{-MNT})_3]^{2-}$, were present and formed molecular ions similar to the homocubane cluster, we would expect to observe a peak at *m*/*z* 1402 corresponding to the addition of three *n*-Bu_4N^+ groups to the dianion. There is no evidence of any peak in this region of the positive ion spectrum; hence this species may not exist. A peak at *m*/*z* 2029, which would correspond to the addition of five *n*-Bu_4N^+ groups to the tetraanion, is again not present, but we do observe the fragment peak $\{Cu_4[S_2P(OR)_2]_3\}^+$ from the positive FAB mass spectra of the centered-cubane clusters, $Cu_8S_{12}X$ (though this may be due to an impurity, as $\{Cu_4[S_2P(OR)_2]_4\}$is a starting material, and not to a fragment of the cubane cluster) [17b]. The charge of the cluster itself may play a role in determining the fragment pattern of the mass spectrum.

These results further demonstrate the general utility of mass spectrometry and specifically the wide versatility of ^{252}Cf-PDMS for confirming the composition of metal cluster complexes. It also poses some interesting questions concerning the gas phase chemistry of these types of clusters. Although PDMS has now largely been replaced by other commercially available methods such as MALDI and ESI [19], we would expect that these methods could be used with similar success and results to study this class of metal clusters based on the many reports of other types of metal clusters described in the recent literature [6]. The field of cluster chemistry is broadly encompassing new frontiers in inorganic chemistry. Techniques for characterizing the formulation and structure of a large metal cluster are often hindered by difficulties in preparing crystals suitable for XRD studies. Other techniques that are widely used, such as NMR and IR spectroscopy, often fail to detect the presence of similar impurities. Although these techniques (and others) must be used to ultimately determine the structure of a metal cluster compound, mass spectrometry has a useful niche as a means for rapidly confirming the product composition in advance of more detailed structural studies.

Acknowledgements

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