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Secondary Ion Mass Spectrometry of Nonvolatile Isocyanide Complexes of Silver(I) and Copper(I)

LISA D. DETTER, R. G. COOKS* and R. A. WALTON*

Department of Chemistry, Purdue University, West Lafayette, Ind. 47907, U.S.A.

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Abstract

A series of silver and copper coordination complexes has been studied using secondary ion mass spectrometry (SIMS). Results are presented for the monomeric silver(I) complexes $[Ag(CNR)_4]X$, where R = cyclohexyl for $X = ClO_4^-$, and R = methyl or t-butyl for $X = PF_6^-$. Likewise, Cu(I) complexes $[Cu(CNR)_4]PF_6$, where R = methyl, t-butyl, or cyclohexyl, were examined. The presence of AgL_2^+ (L represents the intact RNC ligand) and the absence of AgL_3^+ and AgL_4^+ species attests to the gas phase stability of two-coordinate silver(I). Similar results to these were obtained for the Cu(I) complexes, with the exception of $[Cu(CNCH_3)_4]PF_6$ whose spectrum contains CuL_4^+, CuL_3^+, CuL_2^+, CuL^+, and Cu^+ ions. The latter result reflects the enhanced stability of the tetrahedral Cu(I) geometry compared to Ag(I) in the gas phase. Cross labeling experiments and isotopic labeling studies have provided insights into fragmentation mechanisms. Ligand exchange occurs when mixtures are examined. These exchange reactions provide evidence for extensive molecular mixing which can accompany SIMS even under low primary ion dose conditions. Cluster ion formation as well as the observation of α-cleavage of the N–C bonds of RNC ligands have been observed and these results are discussed. Granulated graphite and ammonium chloride were employed to study matrix effects. Granulated graphite enhanced N–C cleavage for the silver complexes but had little effect on the relative abundance of silver cluster ions. On the other hand, copper cluster ions were more sensitive to matrix effects.

Introduction

In recent years, the development of secondary ion mass spectrometry (SIMS) for the analysis of inorganic and organometallic compounds has received increasing attention [1–7]. Continued refinements of the technique have led to increased sensitivity limits for nonvolatile high molecular weight complexes, and the use of liquid matrices (liquid SIMS) has expanded the range of heat-sensitive compounds which can be explored [8–11]. SIMS, along with other desorption ionization techniques such as field desorption (FD) [12], plasma desorption (PD) [13], fast atom bombardment (FAB) [7, 14], and laser desorption (LD) [15], all of which avoid macroscopic vaporization, extends the reach of mass spectrometry [16–18].

In the present study we have examined from two perspectives the behavior of several tetrakis(isocyanide) silver(I) and copper(I) complexes when subjected to ion bombardment. First, the fragmentation behavior of these compounds allowed us to further systemize the correlations being developed between SIMS spectra and the molecular structure of inorganic molecules. Second, we examined in detail these particular complexes, which display unusually high secondary ion yields, intriguing matrix effects, and fragmentation behavior, in order to gain insights into the SIMS mechanisms. The mechanistic questions were addressed through cross labeling and isotopic studies, and through variations in matrix and ion beam parameters. These experiments provide information into the types of chemical reactions which can occur in the plasma region lying immediately above the solid surface during low flux ion bombardment. This study is part of a larger investigation of silver compounds including those containing silver–oxygen and silver–hydrogen interactions [4, 19].

Experimental

Materials

The silver(I) complexes $[Ag(CNC_6H_{11})_4]ClO_4$, $[Ag(CNCH_3)_4]PF_6$ and $[Ag(CNCMe_3)_4]PF_6$ were prepared by stoichiometric addition of a silver perchlorate solution to a stirred solution of the appropriate isocyanide ligand as described in the literature [20]. The analogous copper(I) complexes were prepared in a similar fashion from $[Cu(NCCH_3)_4]PF_6$. Samples were recrystallized and

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*Authors to whom correspondence should be addressed.

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dried under vacuum. A sample of the CD_3NC ligand was prepared by Mr. Mark Reinking of this Department, and the deuterated complex, $[Ag(CNCD_3)_4]ClO_4$, was prepared by the procedure described above. Ammonium chloride was dried and stored under nitrogen. The granulated graphite used had a surface area of 2.50 m^2/g. All chemicals were used without further purification.

Instrumentation

The positive ion SIMS spectra were obtained on a Riber Instrument (Model SQ 156L) using an energy selector, a quadrupole mass filter, a channel-electron multiplier, and pulse counting electronics. A 4.5 keV argon ion beam was used at primary ion currents of 2.0×10^{-9} A/cm^2 or less to minimize beam damage. Operating pressure in the main chamber of the instrument was typically 1×10^{-8} torr or less. Spectra were obtained with the quadrupole scanning rate of 3 s/amu. The region below *m/z* 50 is not reported because of substantial contributions from low molecular weight organic and inorganic surface contaminants. The spectra were reproducible from run to run to within *ca.* 10% of the relative ion abundances. No charge compensation was necessary.

The samples were admixed with 1:1 or 1:10 ratios of granulated graphite or dry ammonium chloride and they were burnished directly onto a sandpaper-etched 1 cm^2 graphite foil (0.25 mm thick, Alfa products) for SIMS analysis. The amount of sample employed was approximately 0.025 g. In general, use of matrices in SIMS analyses increases the intensity of sputtered secondary ions; this observation is discussed in greater detail in the following sections.

Results and Discussion

(a) Positive Ion SIMS Spectra

In the discussion of the SIMS data which follows, the abbreviation L will be used for an intact monodentate methyl, t-butyl, or cyclohexyl isocyanide ligand. Results are given (Table I) for three silver(I) isocyanide complexes of the general formula $[Ag(CNR)_4]X$, where R = methyl or t-butyl when X = PF_6^- and R = cyclohexyl when X = ClO_4^-.

The absence of the higher molecular weight ions AgL_4^+ and AgL_3^+ and presence of AgL_2^+ and AgL^+ (Table I and Fig. 1) reflects the propensity of gas-phase silver(I) complexes to be linear, two-coordinate species [21]. This observation accords with published results for other silver(I) complexes [4], including preliminary data reported previously for $[Ag(CNC_6H_{11})_2]ClO_4$ and $[Ag(CNR)_4]ClO_4$, where R = CMe_3 or C_6H_{11} [4]. Of particular interest is the extent to which N–C bond scission occurs, as indicated by ions such as $[Ag(CNH)]^+$, $[Ag(CNH)_2]^+$, $[AgL(CN)]^+$, $[AgL(CNH)]^+$, and $[AgL_2(CN)]^+$. These ions can be seen in Fig. 1, the SIMS spectrum of $[Ag(CNC_6H_{11})_4]ClO_4$. In all instances, the formation of ions containing CNH (isocyanic acid)* predom-

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*While we write these ions as $[Ag(CNH)]^+$ etc., we cannot easily distinguish between this formulation as the isocyanic acid complex and the alternative hydrocyanic acid form $[Ag(NCH)]^+$. For convenience we shall use the former convention.

TABLE I. SIMS Data for Complexes of the Type $[Ag(CNR)_4]X$ Admixed 1:1 with Granulated Graphite

Fragments[a]	$[Ag(CNC_6H_{11})_4]ClO_4$		$[Ag(CNCH_3)_4]PF_6$		$[Ag(CNCMe_3)_4]PF_6$	
	m/z	*I*[b]	*m/z*	*I*[b]	*m/z*	*I*[b]
Mononuclear species						
AgL_2^+	325	100	189	22	273	4
$[AgL(CNH)]^+$	243	90	175	10	217	15
$[AgL(CN)]^+$	242	8			216	5
AgL^+	216	94	148	64	190	16
$[Ag(cyclohexene)]^+$	189	20				
$[Ag(CNH)_2]^+$	161	63			161	19
$[Ag(CNH)]^+$	134	92	134	10	134	88
Ag^+	107	83	107	100	107	100
$C_6H_{11}^+$	83	40				
Clusters						
$[Ag_2L(CN)]^+$	349	36	281	8	323	5
Ag_2L^+	323	5			297	4
$[Ag_2(CN)_2]^+$	266	6	266	5	266	7
$[Ag_2(CN)]^+$	240	6	240	10	240	7
Ag_2^+	214	8	214	4		

[a] L represents the intact isocyanide ligand. [b] Intensity in percent relative abundance.

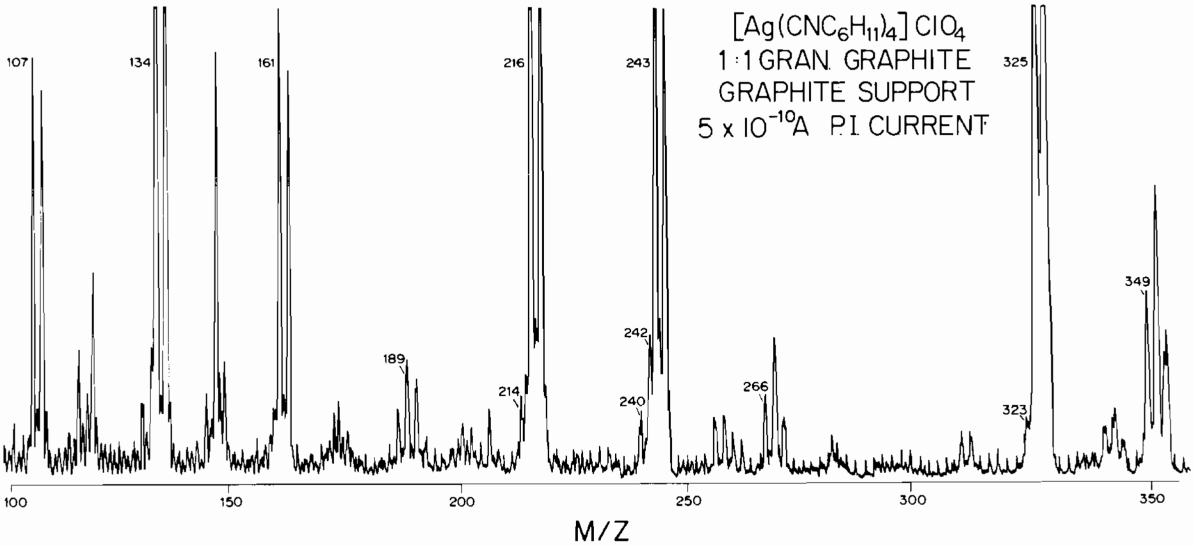

Fig. 1. SIMS spectrum of $[Ag(CNC_6H_{11})_4]ClO_4$ admixed with granulated graphite on graphite foil.

inate at the expense of cyanide-containing species *i.e.* [Ag(CN)]. This accords with previous SIMS results for other isocyanide-containing complexes (mixed nitrosyl-isocyanides of Cr and Mo [2], and mixed carbonyl-isocyanide complexes of Cr [22]) where loss of olefin (formally at least) is a dominant fragmentation pathway and gives mononuclear ions containing the [MCNH] moiety. Other mass spectroscopic techniques may favor the cyano-species [MCN], either through loss of R^+ or homolytic N–C bond cleavage [22, 23], as the primary products of this particular fragmentation path.

In addition to the N–C cleavage products, other ions observed include dinuclear cluster ions $[Ag_2L(CN)]^+$, Ag_2L^+, Ag_2^+, $[Ag_2(CN)_2]^+$, and $[Ag_2(CN)]^+$ (Table I). Cluster ions are commonly observed during the SIMS process as has been reported previously by Busch *et al.* [19] in their studies on silver(I) carboxylates. These latter compounds display abundant ions due to C–C bond cleavage. The C–N cleavage which occurs in the case of the isocyanide complexes studied here, to give the silver clusters $[Ag_2L(CN)]^+$, $[Ag_2(CN)_2]^+$ and $[Ag_2(CN)]^+$, presumably reflects the ability of CN (in contrast to CNH) to enhance the stability of the clusters through the formation of Ag(CN)Ag bridges.

The PF_6^- salts of $[Cu(CNCH_3)_4]^+$, $[Cu(CNCMe_3)_4]^+$, and $[Cu(CNC_6H_{11})_4]^+$ yield SIMS data which closely parallel the silver isocyanide fragmentation patterns (Table II and Fig. 2). The spectrum of each of the copper complexes contains the mononuclear CuL_2^+, CuL^+, and Cu^+ ions formed via successive ligand dissociation. However, $[Cu(CNCH_3)_4]PF_6$ behaves differently (Fig. 2). The intact molecular ion, CuL_4^+, is observed as well as the CuL_3^+, CuL_2^+, CuL^+, and Cu^+ ions. The enhanced stability of the $[Cu(CNCH_3)_4]^+$ ion over its silver counterpart is explained in terms of the preferred tetrahedral geometry for the Cu(I) oxidation state. This stability is enhanced by the fact that loss of a methyl group and especially of a methylene is energetically less favorable than loss of the cyclohexyl or t-butyl groups. All the metal containing ions observed in the spectra of silver and copper complexes are accounted for by a combination of three processes, *viz.*, (i) intact ligand dissociation, (ii) N–C cleavage with or without hydrogen transfer, and (iii) clustering. Note that one feature which distinguishes the cyclohexyl isocyanide complexes from the rest is the presence of the olefin-containing ion $[M(cyclohexene)]^+$ (Tables I and II).

Two general points emerge from a consideration of the SIMS spectra of the silver and copper complexes: first is the extent of fragmentation which occurs from cleavage within ligands. This suggests that relatively large energies are involved in the bond breaking processes. The energy demands are particularly evident from the behavior of $[Ag(CNCH_3)_4]PF_6$ where N–C cleavage does not occur as readily as for the other Ag isocyanides. Thus, the relative abundances of the $[M(CNH)]^+$ and $[M(CNH)_2]^+$ ions (where M = Cu and Ag) are considerably lower for the methyl isocyanide derivatives than for the analogous cyclohexyl and t-butyl isocyanide complexes. This suggests that N–C cleavage via olefin elimination may be a much more favored fragmentation pathway in the case of the latter species. Second, the types of cluster ions generated implies that considerable intermolecular mixing accompanies generation of the spectra. The bond forming process associated with cluster ion formation may be occurring simultaneously with these processes.

The dinuclear clusters, C_2A^+, (where C represents a cation and A an anion) may arise by self-cationiza-

TABLE II. SIMS Data for Complexes of the Type $[Cu(CNR)_4]X$ Admixed 1:1 with Granulated Graphite

Fragments[a]	$[Cu(CNC_6H_{11})_4]PF_6$		$[Cu(CNCH_3)_4]PF_6$		$[Cu(CNCMe_3)_4]PF_6$	
	m/z	I[b]	m/z	I[b]	m/z	I[b]
Mononuclear species						
CuL_4^+			227	16		
CuL_3^+			186	13		
CuL_2^+	281	58	145	71	229	35
$[CuL(CNH)]^+$	199	84	131	16	173	53
CuL^+	172	45	104	100	146	13
$[Cu(cyclohexene)]^+$	145	8				
$[Cu(CNH)_2]^+$	117	84			117	100
$[Cu(CNH)]^+$	90	55	90	16	90	56
$C_6H_{11}^+$	83	55				
Cu^+	63	100	63	88	63	80
$C_4H_9^+$					57	70
Clusters						
$[Cu_2L_2(CN)]^+$	370	11	234	13		
$[Cu_2L(CN)_2]^+$	287	8				
$[Cu_2L(CNH)]^+$	261	5				
$[Cu_2L(CN)]^+$			193	25		
$[Cu_2(cyclohexene)]^+$	208	18				
$[Cu_2(CNH)_2(CN)]^+$	206	18				
$[Cu_2(CNH)(CN)]^+$	179	28			179	13
$[Cu_2(CN)]^+$	152	16	152	25	152	17

[a] L represents the intact isocyanide ligand. [b] Intensity in percent relative abundance.

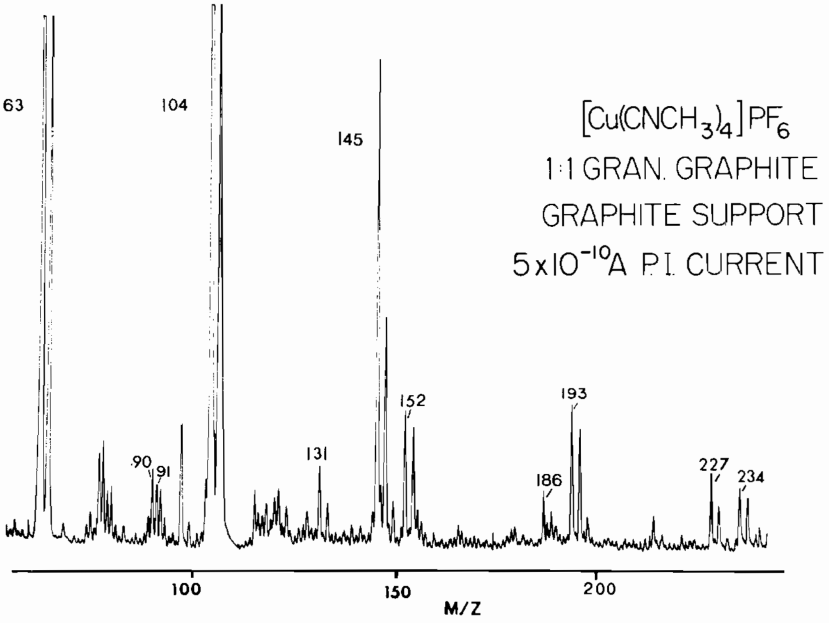

Fig. 2. SIMS spectrum of $[Cu(CNCH_3)_4]PF_6$ admixed with granulated graphite on graphite foil.

tion or from the fragmentation of larger cluster species. Busch *et al.* [19] analyzed silver clusters by tandem mass spectrometry and concluded that many of the lower mass ions originated from the intact C_2A^+ ion, where C is the cation, for example $(Ag_2benzoate)^+$. Clusters of the isocyanide complexes may fragment via similar mechanisms in which case they have the potential to dissociatively rearrange to form metal–metal bonded species. To study Ag and Cu cluster formation in more detail,

TABLE III. SIMS of Mixtures (1:1:1) of $[Cu(CNCH_3)_4]PF_6$, $[Ag(CNC_6H_{11})_4]ClO_4$ and Granulated Graphite on Graphite Foil[a]

m/z	Identity[b]	*I*[c]
Copper species		
281*	$[Cu(CNCy)_2]^+$	28
213*	$[Cu(CNCH_3)_3(CNH)]^+$ and $[Cu(CNCy)(CNCH_3)]^+$	10
199*	$[Cu(CNCy)(CNH)]^+$	44
172*	$[Cu(CNCy)]^+$ and $[Cu(CNCH_3)_2(CNH)]^+$	12
145	$[Cu(CNCH_3)_2]^+$	9
143	$[Cu(CNH)_2(CN)]^+$	12
131	$[Cu(CNCH_3)(CNH)]^+$	21
117	$[Cu(CNH)_2]^+$	62
104	$[Cu(CNCH_3)]^+$	21
90	$[Cu(CNH)]^+$	52
63	Cu^+	100
206	$[Cu_2(CNH)_2CN)]^+$	6
179	$[Cu_2(CNH)(CN)]^+$	4
Silver species		
325	$[Ag(CNCy)_2]^+$	4
261	$[Ag(CNCy)(CNH)(H_2O)]^+$	3
243	$[Ag(CNCy)(CNH)]^+$	4
216*	$[Ag(CNCy)]^+$ and $[Ag(CNCH_3)_2(CNH)]^+$	7
189*	$[Ag(CNCH_3)_2]^+$	2
161	$[Ag(CNH)_2]^+$	4
134	$[Ag(CNH)]^+$	22
107	Ag^+	62

[a]Mixed ligand or cross labeled fragments are denoted by an asterisk. [b]Cy represents the cyclohexyl group, (C_6H_{11}). [c]Intensity in percent relative abundance.

TABLE IV. SIMS of Mixtures (1:1:1) of $[Cu(CNC_6H_{11})_4]PF_6$, $[Ag(CNCH_3)_4]PF_6$ and Granulated Graphite on Graphite Foil[a]

m/z	Identity[b]	*I*[c]
Copper species		
281	$[Cu(CNCy)_2]^+$	100
213*	$[Cu(CNCH_3)_3(NCH)]^+$ and $[Cu(CNCy)(CNCH_3)]^+$	41
199	$[Cu(CNCy)(NCH)]^+$	52
172*	$[Cu(CNCy)]^+$ and $[Cu(CNCH_3)_2(CNH)]^+$	14
145*	$[Cu(CNCH_3)_2]^+$	27
131*	$[Cu(CNCH_3)(CNH)]^+$	78
117	$[Cu(CNH)_2]^+$	83
104*	$[Cu(CNCH_3)]^+$	37
90	$[Cu(CNH)]^+$	29
63	Cu^+	67
Silver species		
325*	$[Ag(CNCy)_2]^+$	100
257*	$[Ag(CNCH_3)(CNCy)]^+$	24
243*	$[Ag(CNCy)(CNH)]^+$	25
216*	$[Ag(CNCy)]^+$ and $[Ag(CNCH_3)_2(CNH)]^+$	51
189	$[Ag(CNCH_3)_2]^+$	14
175	$[Ag(CNCH_3)(CNH)]^+$	25
161	$[Ag(CNH)_2]^+$	24
148	$[Ag(CNCH_3)]^+$	49
134	$[Ag(CNH)]^+$	85
107	Ag^+	83
348	$[Ag_2(CNCH_3)_2(CN)_2]^+$	12
266	$[Ag_2(CN)_2]^+$	5

[a]Mixed ligand or cross labeled fragments are denoted by an asterisk. [b]Cy represents the cyclohexyl group (C_6H_{11}). [c]Intensity in percent relative abundance.

the primary ion current density was increased from approximately 1×10^{-10} A/cm^2 to 1×10^{-9} A/cm^2. This variation caused the relative abundance of the clusters to decrease and the fragments which result from consecutive ligand dissociation to increase. If a gas phase bimolecular reaction was the source of clustering, the higher primary ion current might have caused the opposite results. This implies that the bimetallic ions C_2A^+ are derived directly from the substrate rather than produced from reactions like self-cationization.

(b) *Cross Labeling and Isotopic Labeling Studies*

The mechanisms operating for monomer and cluster ion production in SIMS are not clear. As discussed above, the clusters observed in this study may originate via structural reorganization on the substrate followed by dissociation in the selvedge. Alternatively, the clusters may form in the selvedge region via a recombination mechanism. To gain more insight into the chemical processes which are occurring, cross labeling and isotopic labeling experiments were undertaken. SIMS results for the 1:1 mixtures of $[Cu(CNC_6H_{11})_4]PF_6$ and $[Ag(CNCH_3)_4]PF_6$ as well as $[Cu(CNCH_3)_4]PF_6$ and $[Ag(CNC_6H_{11})_4]ClO_4$ show cross labeled ligand products (Tables III and IV). For both mixtures (Figs. 3 and 4), recombination of Ag^+ and Cu^+ ions with neutral ligands and ligand fragments occurs in the selvedge region as suggested by the nature of the mixed and cross labeled fragments which are present. No general preference for one metal over the other is observed. The presence of the cross labeled products proves that a considerable degree of metal–ligand exchange occurs, a phenomenon that we have observed previously in the case of the SIMS of mixtures of transition metal β-diketonate complexes [3].

Both mixtures contained abundant Ag^+ and Cu^+ ions. Some of the most abundant ions in these mixtures are derived from the recombination of the $C_6H_{11}NC$ ligand (Tables III and IV) with M^+ ions

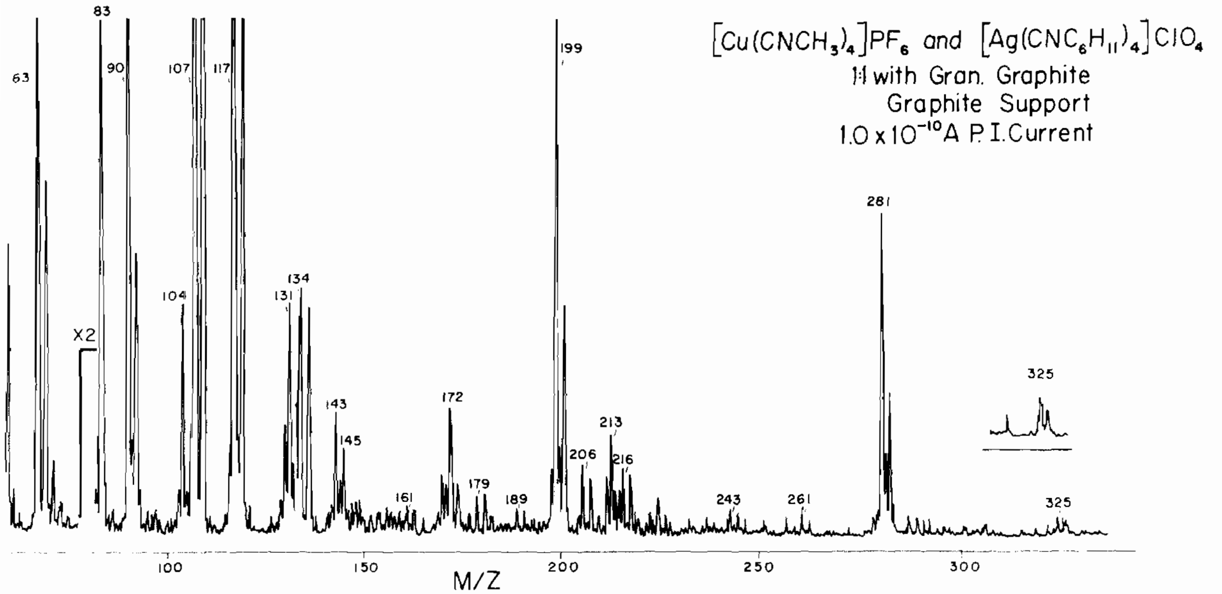

Fig. 3. SIMS spectrum of a 1:1:1 mixture of $[Cu(CNCH_3)_4]PF_6$, $[Ag(CNC_6H_{11})_4]ClO_4$ and granulated graphite on graphite foil.

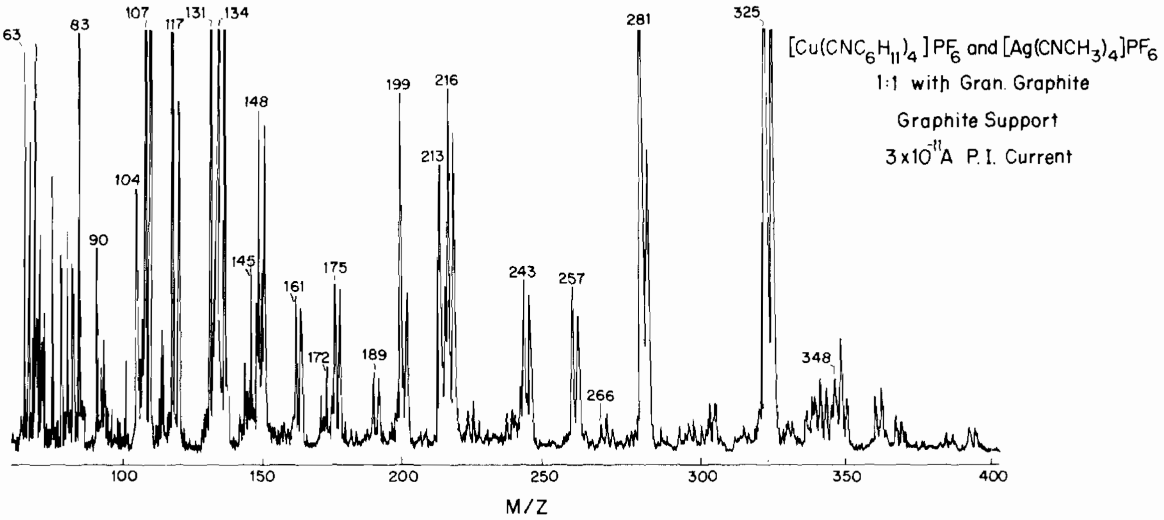

Fig. 4. SIMS spectrum of a 1:1:1 mixture of $[Cu(CNC_6H_{11})_4]PF_6$, $[Ag(CNCH_3)_4]PF_6$ and granulated graphite on graphite foil.

and/or from ligand dissociation of the molecular ion. Among other species in relatively large relative abundance were $[Cu(CNH)_2]^+$, $[Cu(CNH)]^+$ and $[Ag(CNH)]^+$, all of which resulted from N–C cleavage. While N–C cleavage reactions were generally as prevalent as those encountered in the individual components (except in the case of $[Ag(CNC_6H_{11})_4]ClO_4$, Table III), the abundance and formation of clusters is greatly reduced in the mixtures as compared to the single component runs. The reason for the latter observation is unclear at present.

In the general context of the preceding metal–ligand exchange phenomenon, we note that in some systems there is evidence for the incorporation of adventitious water into some of the ions detected in the SIMS study. Such is the situation in the case of the mixture of $[Cu(CNCH_3)_4]PF_6$ and $[Ag(CNC_6H_{11})_4]ClO_4$ (Fig. 3) where we have evidence for ions such as $[Ag(CNC_6H_{11})(CNH)(H_2O)]^+$ (*m/z* 261, 263), $[Ag(CNH)_3(H_2O)]^+$ (*m/z* 206, 208), $[Ag(CNH)_2(H_2O)]^+$ (*m/z* 179, 181), $[Cu_2(CN)(H_2O)]^+$ (*m/z* 170, 172, 174), $[Cu_2(CNH)(CN)(H_2O)]^+$ (*m/z* 197, 199, 201), and $[Cu_2(CNH)_2(H_2O)]^+$ (*m/z* 198, 200, 202). The incorporation of water and other small molecules has been previously observed in FAB and low temperature SIMS studies. For instance, Miller *et al.* [24] used negative FABMS to look at stannous chloride from an HCl-doped

TABLE V. A Comparison of the SIMS of $[Ag(CNCD_3)_4]ClO_4$ and $[Ag(CNCH_3)_4]PF_6$[a]

Fragments	$[Ag(CNCD_3)_4]ClO_4$		$[Ag(CNCH_3)_4]PF_6$	
	m/z	I^b	*m/z*	I^b
Mononuclear species				
$[Ag(CNCD_3)_2]^+$	195	24		
$[Ag(CND)_2]^+$	163	2		
$[Ag(CNCH_3)_2]^+$			189	22
$[Ag(CNCD_3)]^+$	151	80		
$[Ag(CNCH_3)]^+$			148	64
$[Ag(CND)]^+$	135	5		
$[Ag(CNH)]^+$			134	10
Ag^+	107	100	107	100
Clusters				
$[Ag_2(CN)_2]^+$			240	10
Ag_2^+	214	5	214	4

[a] Samples admixed 1:1 with granulated graphite. [b] Intensity in percent relative abundance.

glycerol matrix. The spectrum showed ions corresponding to $SnCl_2$, $SnCl_3$, and $SnCl_3 \cdot H_2O$. The contribution of water coordination to the stabilization of charged clusters may be analogous to the results observed by Michl and coworkers [25] for simple molecular solids such as dinitrogen and carbon monoxide at cryogenic temperatures. The study of such clusters may lend some insights into the types of solvated ion-solvent interactions which can occur during room temperature SIMS measurements.

Isotopic labeling studies were undertaken using samples of $[Ag(CNCD_3)_4]ClO_4$ (admixed 1:1 with graphite) to determine the origin of the hydrogen atom present in the [MCNH] moiety (see Table V and Fig. 5). For both the deuterated and the non-deuterated methyl isocyanide complexes, the AgL_2^+, AgL^+, and Ag^+ ions are observed, where L represents the intact ligand. It should be emphasized that the deuterated ligands remain fully intact during normal ligand dissociation and that N–C cleavage products contain only deuterium, namely, $[Ag(CND)_2]^+$ and $[Ag(CND)]^+$. This study strongly implicates the source of hydrogen/deuterium to be from the intact ligand as opposed to other sources such as gas phase ion–molecule recombinations or from substrate impurities.

As a further mechanistic check we also studied a 1:1:1 mixture of $[Cu(CNCMe_3)_4]PF_6$, $[Ag(CNCD_3)_4]ClO_4$, and granulated graphite. As expected from the results of the SIMS analysis of the mixtures discussed earlier, both mixed ligand and cross labeled products are observed; examples include $[Cu(CNCMe_3)(CNCD_3)]^+$ (*m/z* 190), $[Ag(CNCD_3)(CNCMe_3)]^+$ (*m/z* 234), and $[Ag(CNCMe_3)]^+$ (*m/z* 190). Based upon our SIMS results for $[Ag(CNCD_3)_4]ClO_4$ (Table V and Fig. 5), the presence of $[Cu(CND)]^+$ (*m/z* 91) and $[Ag(CNH)]^+$ (*m/z* 134) ions in the spectrum of the mixture is best explained in terms of ion-molecule reactions occurring between intact RNC ligands and Cu^+ or Ag^+ ions in the selvedge region, followed by N–C bond cleavage.

Matrix Effects

Previously, a preliminary study of the SIMS of $[Ag(CNCMe_3)_4]ClO_4$ had shown [4] that granulated graphite or graphite foil was the matrix/support material of choice for obtaining the most structurally

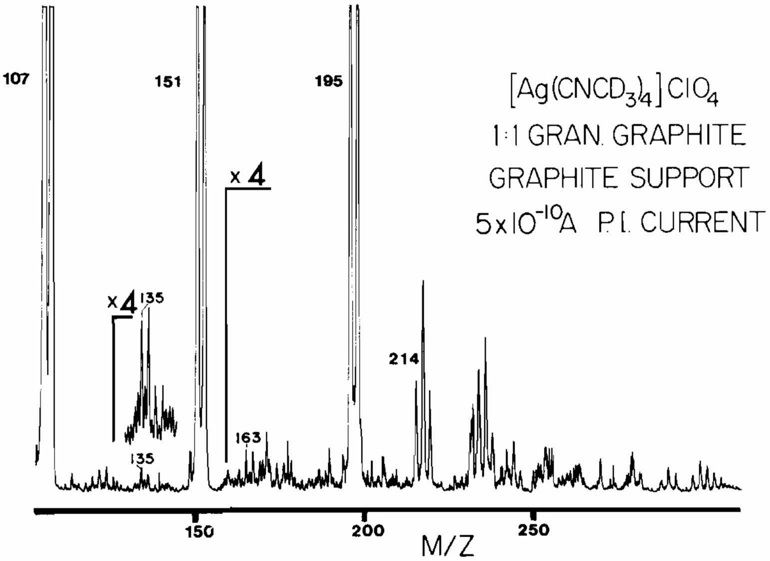

Fig. 5. SIMS spectrum of $[Ag(CNCD_3)_4]ClO_4$ admixed with granulated graphite on graphite foil.

TABLE VI. Matrix Effects of Granulated Graphite on Cluster Formation in the SIMS of $[Ag(CNC_6H_{11})_4]ClO_4$ and $[Cu(CNC_6H_{11})_4]PF_6$[a]

Fragments	$[Ag(CNC_6H_{11})_4]ClO_4$			$[Cu(CNC_6H_{11})_4]PF_6$		
	No GG	With GG	GG/No GG[b]	No GG	With GG	GG/No GG[b]
Mononuclear species						
ML_2^+	100	100	1.0	24	53	2.2
$[ML(CNH)^+]$	90	90	1.0	22	34	1.6
$[ML(CN)]^+$	35	26	0.7			
ML^+	88	90	1.0	19	20	1.0
$[M(cyclohexene)]^+$	17	23	1.4	12		
$[M(CNH)_2]^+$	47	82	1.7	76	84	1.1
$[M(CNH)]^+$	58	92	1.6	83	54	0.65
M^+	78	73	0.9	100	100	1.0
$C_6H_{11}^+$		42		78	55	0.7
Clusters						
$[M_2L_2(CN)]^+$					9	
$[M_2L(CN)_2]^+$					2	
$[M_2L(CNH)]^+$					6	
$[M_2L(CN)]^+$	23	33	1.4			
M_2L^+	17	15	0.9			
$[M_2(cyclohexene)]^+$					12	
$[M_2(CNH)_2(CN)]^+$				6	8	1.3
$[M_2(CNH)(CN)]^+$				10	12	1.2
$[M_2(CN)_2]^+$	13	15	1.2			
$[M_2(CN)]^+$	13	15	1.2	13	17	1.3
M_2^+	18	15	0.8			

[a] GG represents granulated graphite. Numbers represent percent relative abundance. M represents copper or silver and L the intact isocyanide ligand. [b] Ratio of ion abundances using a granulated graphite matrix *vs.* the neat sample.

informative spectrum. In the present study on a much wider range of isocyanide complexes, we have found that a matrix of NH_4Cl or granulated graphite yield similar spectral results when used in conjunction with a graphite foil. However, the granulated graphite was preferred in this study because the compounds adhered more strongly when applied to the foil. The idea of using a matrix from which to ionize molecules in SIMS was introduced by Michl and co-workers [26] who used a frozen argon matrix for the analysis of hydrocarbons. Table VI shows the matrix effects on secondary ion yields and clustering reactions for $[Ag(CNC_6H_{11})_4]ClO_4$ and $[Cu(CNC_6H_{11})_4]PF_6$. These spectra were recorded using very similar instrumental parameters; comparable studies were carried out on the other complexes. The N–C cleavage reactions were enhanced for $[Ag(CNC_6H_{11})_4]ClO_4$ (and also for $[Ag(CNCH_3)_4]PF_6$ in a separate experiment) when admixed with granulated graphite as suggested by the increased relative abundances of $[Ag(CNH)]^+$ and $[Ag(CNH)_2]^+$. In the case of $[Ag(CNCMe_3)_4]ClO_4$, it was found that N–C cleavage reactions were not affected significantly by the matrix. Simple ligand dissociations of the three Ag isocyanide complexes were unchanged by the granulated graphite. Unlike the behavior of the silver salts, the abundances of the $[Cu(CNH)]^+$ and $[Cu(CNH)_2]^+$ ions were not significantly enhanced by the addition of granulated graphite in the case of the three copper isocyanide complexes. Data for $[Cu(CNC_6H_{11})_4]PF_6$ are presented in Table VI. However, the simple ligand dissociations were enhanced, especially in the case of $[CuL_2]^+$.

Whereas the relative abundance of silver cluster ions was not greatly influenced by the matrix (NH_4Cl or granulated graphite) as can be seen from a comparison of data in Tables I and VI, the copper cluster ions were much more sensitive to matrix effects. As Table VI shows, many of the clusters visible with the granulated graphite matrix were not detected when the compound solely was applied to the graphite foil.

In summary, the role of the granulated graphite and NH_4Cl matrices is not well understood in SIMS. It is apparent that fragmentations are affected when matrices are used in conjunction with these copper and silver isocyanide complexes. However, the sensitivity of these results to the exact experimental conditions used, and the accompanying difficulty of reproducing the intensity data from one run to another preclude any meaningful quantitation of these observations at the present time.

Concluding Remarks

The thermal spike model of SIMS emission [27] is an attractive if very approximate explanation for the phenomena observed in this paper. The similarity with the behavior of simple molecules such as nitrogen oxides in frozen rare gas matrices [28, 29] is worthy of emphasis.

The degree of ligand mixing observed in the inorganic complexes is large but nevertheless more restricted than in the nitrogen oxides. Ligands exchange more or less freely between metal centers but ligand dissociation by olefin elimination is apparently intramolecular. It is not possible, from these results, to determine the point at which dissociation occurs. That is, it is not possible to distinguish molecular rearrangement in a large cluster, after ejection from the surface, from reorganization occurring at the interface. It is clear, however, that cluster formation is an important feature of the SIMS spectra of these complexes and, accordingly, it decreases the information obtainable regarding isolated mononuclear complexes in circumstances like these where intermolecular forces are significant.

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