Secondary-Ion Mass Spectra of Nonvolatile Silver Complexes

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A series of silver coordination complexes has been studied with secondary-ion mass spectrometry. The results are presented here for the monomeric silver(I) complexes [Ag(am)$_2$]NO$_3$, where am = 1,10-phenanthroline or 2,2'-bipyridyl, [Ag(PR$_3$)$_4$]X, where R$_3$ = Et$_3$, n-Pr$_3$, or Me$_2$Ph for X = NO$_3$ and R$_3$ = Ph$_3$ for X = ClO$_4$, [Ag(SC(NHR)$_2$)$_2$]NO$_3$, where R = H or Me, and [Ag(CNR)$_n$]ClO$_4$, where R = C$_6$H$_{11}$ for n = 2 and R = C$_6$H$_{11}$ or CMe$_3$ for n = 4. The silver(II) complexes [Ag(bpy)$_2$]S$_2$O$_8$ and [Ag(py)$_4$]S$_2$O$_8$ were examined in addition to the polymeric pyrazine complexes Ag(pyz)NO$_3$ and Ag(pyz)$_2$S$_2$O$_8$. Graphite was found to be the most useful support material for the analysis of these complexes. The presence of AgL$_2^+$ and the lack of AgL$_3^+$ and AgL$_4^+$ species in the resulting SIMS spectra attest to the stability of two-coordinate silver in the gas phase. The silver(I) complex of the rigid, bidentate phenanthroline ligand, however, is an exception, and the four-coordinate intact cation is observed.

Introduction

Secondary-ion mass spectrometry (SIMS) has been successfully applied in the past to the characterization of a variety of transition-metal coordination compounds and organometallics, typically resulting in characteristic, straightforward mass spectra of these nonvolatile materials.[1-3] The fundamentals and applications of molecular SIMS have been described in detail.[4-6] SIMS employs energetic ions (e.g., 4-keV Ar$^+$) as probe particles. The secondary ions ejected upon surface bombardment are collected and subsequently mass analyzed by using conventional methods. Although formally a surface-sensitive technique, bulk analysis can also be easily performed.

Secondary-ion mass spectrometry has been applied here to the study of silver complexes. The mass spectra of nonvolatile coordination compounds of silver with nitrogen-, phosphorus-, and sulfur-containing ligands in addition to several isocyanide complexes of silver are presented. This is part of a larger investigation of silver compounds including those containing silver–oxygen interactions. These studies are of relevance to the role of such species in heterogeneous catalysis, especially the characterization by SIMS of intermediates in the silver-catalyzed oxidation of alkenes.[7] The species reported here are of additional interest due to their often complex solid-state geometries. Although linear two-coordinate and tetrahedral four-coordinate arrangements predominate, silver complexes are known to display a wide range of coordination numbers;[8] structures of these complexes are often of very low symmetry and are frequently polymeric.[9] It was, therefore, of interest to look at the mass spectra of such species directly from the solid state, as is possible with SIMS, in order to examine potential correlations between the mass spectrum and the structure of the analyte.

Experimental Section

Materials. The silver(I) complexes Ag(pyz)NO$_3$,[10] [Ag(phen)$_2$]NO$_3$,[11] [Ag(bpy)$_2$]NO$_3$,[11] [Ag(PR$_3$)$_4$]NO$_3$,[12] where R$_3$ = Et$_3$,

n-Pr$_3$, or Me$_2$Ph, and [Ag(SC(NHR)$_2$)$_2$]NO$_3$, where R = H or Me,[13] were prepared by the stoichiometric addition of a silver nitrate solution to a stirred solution of the appropriate ligand as described in the literature. The phosphine complexes were prepared by a procedure analogous to that described for the p-tolylphosphine derivative;[12] these complexes were examined as oils. The complexes [Ag(PPh$_3$)$_4$]NO$_3$,[14] [Ag(CNC$_6$H$_{11}$)$_2$]ClO$_4$, and [Ag(CNR)$_4$]ClO$_4$, where R = CNCMe$_3$ or CNC$_6$H$_{11}$, were provided by Andrew Bell. The silver(II) complexes [Ag(py)$_4$]S$_2$O$_8$,[15] Ag(pyz)$_2$S$_2$O$_8$,[16] and [Ag(bpy)$_2$]NO$_3$[17] were prepared by the addition of K$_2$S$_2$O$_8$ to the ligand solution prior to the addition of aqueous silver nitrate as described in the literature. Samples were recrystallized as directed and then dried.

The ligand abbreviations used are as follows: pyz = pyrazine, phen = 1,10-phenanthroline, bpy = 2,2'-bipyridyl, and py = pyridine.

Instrumentation. The SIMS spectra were obtained on a Riber instrument (Model SQ 156L) in the positive-ion mode using an energy selector, a quadrupole mass filter, a channeltron electron multiplier, and pulse-counting electronics. A 4-keV argon ion beam was used, and the primary ion current was typically 10^{-10} A or less and was focused to a beam size of 0.1 cm^2. Main-chamber pressure during analysis was on the order of 1 × 10^{-8} torr or less. No charge compensation was necessary.

The samples were burnished directly onto a sandpaper-etched 1-cm^2 graphite foil (Alfa Products, 0.25 mm thick) for SIMS analysis. When samples were run from a matrix, this was present in an approximate 10-fold excess and physically mixed with the sample by using a mortar and pestle.

Results and Discussion

Matrix Effects. As previously reported,[2] the SIMS of [Ag(CNCMe$_3$)$_4$]ClO$_4$ from an ammonium chloride matrix off platinum foil failed to produce spectral evidence for this complex, except for the appearance of Ag$^+$. On the other hand, such analysis conditions have been used successfully to generate complete mass spectra of chromium and molybdenum isocyanide complexes and have been routinely employed for the study of coordination compounds of a variety of different metal centers.[1] Analysis of [Ag(CNCMe$_3$)$_4$]ClO$_4$ from graphite foil, however, produced Ag$^+$, AgL$^+$, and AgL$_2^+$ (where L = CNCMe$_3$) in addition to fragments of these ions—see the appropriate figure given in ref 1. Graphite has also been used successfully as a support material in previous SIMS analyses of nucleosides.[18] This prompted investigation into the matrix effect for [Ag(CNCMe$_3$)$_4$]ClO$_4$ in order to discern optimum analysis conditions for this and other silver complexes.

The *tert*-butyl isocyanide–silver complex was analyzed neat from platinum foil and from a sodium chloride matrix on Pt foil in addition to the above procedure using an ammonium

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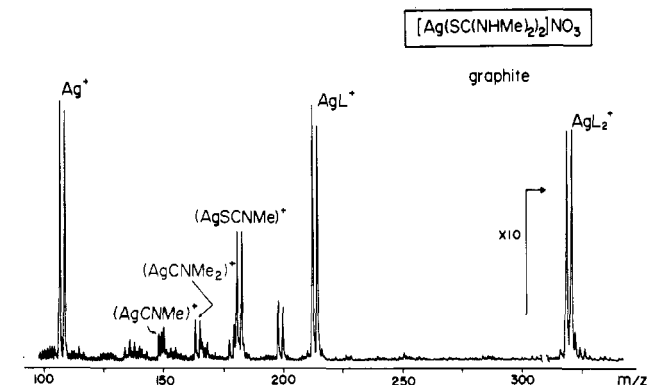
Figure 1. SIMS spectrum of the dimethylthiourea derivative of silver(I), $[Ag(SC(NHMe)_2)_2]NO_3$, on graphite showing the intact cation and additional fragmentation.

Figure 2. SIMS spectrum of $[Ag(phen)_2]NO_3$ on graphite showing the presence of the intact cation.

chloride matrix supported on Pt, in order to discern possible deleterious effects due to the NH_4Cl matrix. In each case, only Ag^+ is observed. A series of covalent matrices including silicon, sulfur, molybdenum disulfide, 1,10-phenanthroline, coronene, and 18-crown-6, all in the form of powders, also failed to produce any ions, except Ag^+, that were characteristic of this complex. Use of a graphite matrix, however, yielded structurally diagnostic ions including Ag^+, AgL^+, and AgL_2^+. Similar results were achieved whether the sample was burnished directly onto the graphite surface, deposited from solution, or admixed with powdered graphite and pressed into a pellet or this mixture burnished onto platinum foil. Corresponding observations were also made for the complexes $[Ag(phen)_2]NO_3$ and $[Ag(bpy)_2]NO_3$, and consequently, all further analyses were accomplished by burnishing the analyte directly onto graphite foil. No other matrix material tested produced the excellent results achieved by using graphite, but the reason for the advantage of a graphite support for the analysis of these silver complexes is not apparent.

SIMS Results. In subsequent discussions of the SIMS results, the abbreviation L will be used for an intact monodentate ligand while L' will be the abbreviation for a bidentate ligand.

The thiourea derivatives of silver, $[Ag(SC(NHR)_2)_2]NO_3$, where R = H or Me, yield SIMS spectra characteristic of the analyte. For each complex, the intact cation is observed as AgL_2^+. Fragmentation to give AgL^+ readily occurs in each case with further fragmentation to give ions such as $[Ag(SCNMe)]^+$, $[Ag(CNMe_2)]^+$, and $[Ag(CNMe)]^+$, as shown for the dimethylthiourea derivative in Figure 1.

The phosphine derivatives $[Ag(PR_3)_4]X$, where $R_3 = Et_3$, n-Pr_3, or Me_2Ph for $X = NO_3$ and $R_3 = Ph_3$ for $X = ClO_4$, also yield simple, characteristic SIMS spectra. In each case, Ag^+, AgL^+, and AgL_2^+ (where L is the phosphine ligand) are observed as shown in Figure S1 (supplementary material) for the dimethylphenylphosphine derivative. There was, in no instance, evidence for AgL_3^+ or the intact cation AgL_4^+. The ions $(PR_3 + H)^+$ and $(PR_3 - H)^+$, in addition to PPh_3^+, P-$(C_6H_4)_2^+$, and $P(C_6H_5)_2^+$ in the case of the triphenylphosphine derivative only, are also observed. Similar ions due to the phosphine ligands have been observed previously for molybdenum and rhenium phosphine complexes[19] and for organic phosphonium salts.[20]

The isocyanide complexes $[Ag(CNC_6H_{11})_2]ClO_4$ and $[Ag(CNR)_4]ClO_4$, where $R = C_6H_{11}$ or CMe_3, all yield similar SIMS spectra. The ions Ag^+, AgL^+, and AgL_2^+ (where L is the isocyanide ligand) characterize the analyte as shown for
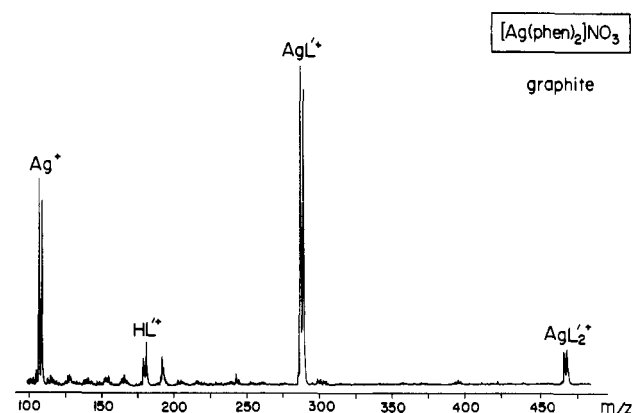
the bis(cyclohexyl isocyanide) derivative in Figure S2 (supplementary material). Fragmentation to give $Ag(HCN)^+$, $Ag(HCN)_2^+$, and $AgL(HCN)^+$ occurs in each case. Again, AgL_3^+ and the molecular cation AgL_4^+ are not observed.

The nitrogen-containing bidentate ligands 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy) form four-coordinate silver complexes. The SIMS spectrum of $[Ag(phen)_2]NO_3$ characterizes this complex by $(L' + H)^+$, Ag^+, AgL'^+, and AgL'_2^+, where L' = phen, as shown in Figure 2. The analogous bipyridyl complex yields a similar spectrum except that AgL'_2^+ is not observed. An identical spectrum is obtained for the silver(II) complex $[Ag(bpy)_2]S_2O_8$, suggesting facile reduction to the silver(I) unipositive cation. The silver(II) pyridine complex $[Ag(py)_4]S_2O_8$, however, exhibits a spectrum rich in fragment ions and containing no AgL_n^+ species except for a small amount of AgL^+. Doubly charged species are not commonly observed in SIMS analyses, the reduced form of the intact cation, i.e., $[Ag(py)_4]^+$, is apparently unstable in the gas phase, and extensive fragmentation results. This is consistent with solution studies in which $[Ag(py)_4]ClO_4$ has been isolated but is reportedly unstable with respect to loss of pyridine.[21]

All of the aforementioned silver complexes are monomeric two- and four-coordinate species. The crystal structure of the pyrazine adduct $Ag(pyz)NO_3$, however, shows this compound to be polymeric with each silver atom coordinated to two pyrazine molecules and containing four Ag–O interactions with the nitrate oxygens, making each silver atom formally six-coordinate.[10] The silver(II) pyrazine complex $Ag(pyz)_2S_2O_8$ is also polymeric with each silver atom coordinated to four pyrazine ligands.[16] The SIMS spectrum of $Ag(pyz)_2S_2O_8$ exhibits only the Ag^+ ion. However, both Ag^+ and AgL_2^+ are observed in the SIMS spectrum of $Ag(pyz)NO_3$ as shown in Figure S3 (supplementary material). No evidence of the Ag–O interactions is observed. Note that AgO^+ is, in fact, not observed even when AgO is the analyte[22] or when an oxygen-saturated silver surface is examined;[23] oxide clusters Ag_nO^+ (n = 1–3) were observed, however, in the SIMS analysis of silver nitrate and nitrite salts.[24] This result suggests an equally strong interaction between the metal center and the two bridging pyrazine molecules and a relatively weak interaction between the metal center and the surrounding nitrato groups. It is surprising, however, that only the AgL_2^+ species, with no AgL^+, is observed. This difference between the monomeric and polymeric species can be rationalized as

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a consequence of the expected smaller internal energy of the AgL_2^+ ion generated from the polymer, given the expenditure of internal energy needed to break its strong intramolecular bonds.

Conclusion

Except for the 1,10-phenanthroline derivative, only one- and two-coordinate silver species are observed in the SIMS analyses; no silver species containing three or four monodentate ligands were obtained. This conspicious lack of higher molecular weight ions, as previously suggested,[2] attests to the propensity of silver complexes to be linear, two-coordinate species.[8] The rigid nature of the bidentate phenanthroline ligand precludes a two-coordinate linear geometry and so, not surprisingly, is an exception to the general observation, and the presumably four-coordinate $Ag(phen)_2^+$ is observed.

Graphite appears to be the matrix of choice for the SIMS analysis of these complexes in order to generate the most analytically useful spectra. Even under these conditions, though, molecular weight information could be obtained only for those complexes that contained two ligands coordinated to the silver center. Polymeric silver compounds gave no evidence for the complexity of the solid-state geometry in the SIMS spectrum of the analyte. Nonetheless, characteristic spectra were readily obtained for each of the silver(I) complexes studied here.

Our results demonstrate the successful application of SIMS to the analysis of coordination complexes of silver and, furthermore, indicate the potential of this technique in characterizing surface species formed by the chemisorption of carbon, nitrogen, phosphorus, and sulfur ligands on silver-containing surfaces.

Registry No. [Ag(phen)₂]NO₃, 60939-16-4; [Ag(bpy)₂]NO₃, 33971-93-6; [Ag(PEt₃)₄]NO₃, 86595-09-7; [Ag(P-*n*-Pr₃)₄]NO₃, 86595-11-1; [Ag(PMe₂Ph)₄]NO₃, 86550-04-1; [Ag(PPh₃)₄]ClO₄, 60185-35-5; [Ag(SC(NH₂)₂)₂]NO₃, 33570-47-7; [Ag(SC-(NHMe)₂)₂]NO₃, 86550-02-9; [Ag(CNC₆H₁₁)₂]ClO₄, 86550-06-3; [Ag(CNC₆H₁₁)₄]ClO₄, 86595-13-3; [Ag(CNCMe₃)₄]ClO₄, 86631-61-0; [Ag(bpy)₂]S₂O₈, 28226-64-4; [Ag(py)₄]S₂O₈, 15810-50-1; [Ag(pyz)]NO₃, 86550-08-5; [Ag(pyz)₂]S₂O₈, 33219-39-5; graphite, 7782-42-5.

Supplementary Material Available: Figures S1–S3, showing the SIMS spectra of [Ag(PMe₂Ph)₄]NO₃, [Ag(CNC₆H₁₁)₂]ClO₄, and Ag(pyz)NO₃ (3 pages). Ordering information is given on any current masthead page.

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Solution Chemistry of Lanthanide Complexes. 6. Circularly Polarized Luminescence Studies on Terbium(III) Mixed-Ligand Complexes Containing Chiral α-Hydroxy Carboxylic Acid Ligands

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The complexation of hydroxy carboxylic acids by Tb(III) in a series of ternary complexes was examined by means of circularly polarized luminescence (CPL) spectroscopy. The chirality induced in the Tb(III) ion by L-mandelic, L-lactic, L-argininic, and L-malic acids was followed by studies of their CPL spectra, and perturbations of these spectra induced by the achiral portion of the complex were examined in detail. A series of complexes having the general formula Tb(MDL)₂(HXCA) (MDL = oxydiacetic, iminodiacetic, or 5-sulfosalicylic acids) and Tb(APC)(HXCA) (APC = hexadentate aminopoly-carboxylate ligands) were prepared. The line shapes of the resulting CPL spectra could be used to determine the mode of bonding exhibited by the chiral ligands, and a variety of modes were found to be possible with the L-malic acid ligand. Systematic variation of the concentration of chiral ligand relative to the concentration of either Tb(MDL)₂ or Tb(APC) permitted a calculation of the formation constants corresponding to addition of one molecule of chiral ligand, and these values were found to support the trends established from consideration of the CPL band shape data.

Introduction

The conformation effects associated with coordinated chelate rings of transition-metal complexes have been of interest for some time,[1,2] and clearly chiroptical techniques are best suited for these studies. Analogous studies on chiral lanthanide complexes have not been carried out in as much detail, a situation which is a consequence of the labile nature of the compounds. Nevertheless, the question is quite important as chiral lanthanide compounds are currently the focus of increasing attention.[3]

The weak f–f absorptions of lanthanide compounds precludes the effective use of circular dichroism in the study of chiral lanthanide complexes, but studies of the circularly polarized luminescence emitted by chiral Tb(III) and Eu(III) compounds can provide the necessary information.[4] In our laboratory, we have been able to simplify solution equilibria through the use of mixed-ligand complexes (containing both chiral and achiral ligands) and have been investigating the optical activity observed in a series of Tb(III)[5–11] and Eu(III)[12] compounds. Related studies have been reported by Das Gupta and Richardson.[13] In the present work, we extend the scope

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