National Science Foundation Postdoctoral Fellowship (1980-1981). W.C.L. was supported by a University of Colorado Faculty Fellowship and a J. S. Guggenheim Foundation Fellowship (1981-1982). We thank H. Benton Ellis, Jr., and G. Barney Ellison for the many discussions which led to the source modifications discussed in this paper.

Registry No. $Ni(CO)^-$, 82639-17-6; $Ni(CO)_2^-$, 82639-18-7; $Ni(CO)_3^-$, 51222-94-7; $Ni(CO)_4$, 13463-39-3; Ni(CO), 33637-76-2; $Ni(CO)_2$, 33637-77-3; $Ni(CO)_3$, 26024-55-5.

Observation of Some Transition Metal Complexes in Solution by Electrohydrodynamic Ionization Mass Spectrometry

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Abstract: Direct mass spectral sampling of glycerol solutions of bipyridyl complexes of ruthenium and chromium has been achieved by electrohydrodynamic ionization. The spectra show no evidence of fragmentation, but do reflect the solution chemistry of the complexes. The ruthenium(II) complex ($Ru(bpy)_3^{2+}$) was stable and inert in solution, whereas the chromium(II) complex ($Cr(bpy)_3^{2+}$) underwent both ligand exchange (with Cl^- and glycerol (G)) and oxidation to form a mixture of singly and doubly charged complexes ($Cr(bpy)_3^{2+}$, $Cr(bpy)_2Cl^+$, $Cr(bpy)_2Cl_2^+$, $Cr(bpy)_2(G-2H)^+$, and $Cr(bpy)_2Cl(G-H)^+$). $Zn(bpy)_2Cl^+$ was detected as impurity in the chromium sample. These results suggest that electrohydrodynamic ionization mass spectrometry should be a valuable probe of the solution chemistry of ion-ligand interactions.

Introduction

An important characteristic of the chemistry of transition metal complexes in solution is their ability to exchange ligands with surrounding species, including solvent molecules. The extent of ligand exchange depends on the thermodynamic stability and kinetic lability of the complex, the ligands involved, and the solvent. While the structure and composition of a complex in the solid state may be characterized by a variety of techniques, these properties may change substantially upon dissolution. It is important to know what species actually exist in solution in order to understand the chemistry of the system.

Solution systems are usually characterized by methods such as electron spin resonance, nuclear magnetic resonance, Raman, infrared, and ultraviolet-visible spectroscopy. These spectroscopic techniques relate the energy of various transitions to the structure of the complex. Generally, two or more of these techniques are used complementarily in the characterization process. Nevertheless, the utility of these approaches is somewhat limited for solutions comprised of a mixture of similar species (or species involved in exchange equilibria) whose spectra may not be resolved, but rather represent the average bulk behavior of the mixture.

Many complexes of similar structure (and therefore similar optical spectroscopy) have appreciably different masses. However, despite the broad utility of mass spectrometry for determination of molecular weights and structures, this information cannot be simply obtained for solution systems by conventional mass spectrometric techniques. These techniques sample molecules from gaseous or solid phase with subsequent or concurrent ionization. For example, the application of standard electron impact mass spectrometry (EIMS)[1] to the analysis of thermally labile, nonvolatile samples (such as transition metal complexes) is limited because a large amount of energy is imparted to sample molecules during volatilization and EI ionization. This can grossly affect equilibria and also cause significant fragmentation of molecular ions, often resulting in the loss of molecular weight information. Thus, although the mass spectra obtained from EIMS are often useful for structure determination of analytes, their complexity impedes application to mixture analysis.

Simpler spectra can be obtained using "soft" ionization processes, which promote less fragmentation. Chemical ionization (CI),[2] field ionization (FI),[3] and field desorption (FD)[4] are principal examples. In CI and FI, gaseous analytes are ionized by a reagent gas (CI) or an electric field (FI). Solids and liquids must be heated to vaporize as in EI, reducing the applicability of CI and FI for analysis of thermally labile, nonvolatile samples. As a result, FD is often the ionization process of choice for mass spectrometric analysis of nonvolatiles. In a FD ion source, analyte solution is loaded onto an emitter wire. The solvent is subsequently removed by evaporation. Desorption and ionization are promoted by the application of a high electric field between the emitter and extractor. Unfortunately, it is usually necessary to heat the emitter to several hundred degrees, promoting degradation or decomposition of thermally labile nonvolatile samples. Again, resulting fragment ions complicate direct mixture analysis. Furthermore, as for CI and EI, solvent removal precedes FD ionization and may perturb solution equilibria among species to be characterized.

Another family of soft ionization techniques relies on the inefficiency of energy transfer to internal degrees of freedom upon sample bombardment by energetic photons (laser desorption, LDMS),[5] ions (secondary ion, SIMS),[6] fission fragments (plasma desorption, PDMS),[7] or neutral atoms (fast atom bombardment, FABMS).[8] Of these, all but FABMS have been used primarily for solid samples. For reasons still unclear, FAB ionization is facilitated if the sample is introduced as a glycerol slurry or solution. Thus, of all conventional "soft" ionization methods, FABMS offers the best chance for characterization of solutions. However, appreciable fragmentation always accompanies FAB ionization, which limits applicability for direct mixture analysis.

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By contrast, electrohydrodynamic ionization mass spectrometry (EHMS)[9-11] samples ions directly from solution and has been shown to be an extremely soft ionization process.[9,12-16] The mechanism of this process has been discussed by Stimpson and Evans.[9] The formation of ions occurs in solution via electrolytic dissociation or by ion attachment. The ion attachment process is aided by the addition of an inorganic salt (such as NaI or NaCl), which also assists the ion emission process by increasing the conductivity of the solution. (To promote ion emission, solution conductivity on the order of 10^{-4} Ω^{-1} cm^{-1} is generally required.[12]) Ions are extracted directly from solution by the action of an applied electrostatic field. Ions thus sampled possess little excess internal energy, and there is little or no evidence of fragmentation except for products of solution-phase reactions. Unimolecular decomposition products observed using other ionization techniques have not been detected. Because solution is introduced directly into the ion source, solvents of low volatility have generally been used. Volatile solvents increase the pressure in the ion source, resulting in scattering and/or electrical discharge between the emitter needle and counter electrode. Glycerol has been the solvent of choice for EHMS[12,17] because of its low volatility (vapor pressure = 3×10^{-4} torr at 20 °C) and its good solvent properties. Other solvents used have included diglycerol and ethylene glycol.[17] Since the first development of EHMS by Evans and Hendricks[11] in 1972, it has been applied to the analysis of a variety of thermally labile nonvolatile inorganic,[10,11] organic,[12,13,16] and biochemical[14,15] samples.

Because ions are sampled directly from solution without fragmentation, and therefore reflect solution chemistry products, it was felt that EHMS should be well suited for sampling systems comprised of mixtures of ionic ligand exchange products in solution, provided that glycerol is a suitable solvent for the systems of interest and that added supporting electrolyte can be tolerated. In fact, EHMS has been used for analysis of two kinds of mixtures. Evans and co-workers sampled metals from liquid alloys,[10,11] obtaining semiquantitative information over a wide range of abundances. In work involving true ionic solutions (with glycerol solvent), Cook and co-workers obtained molecular weight distributions with accurate averages from poly(ethylene glycols).[16] Quasimolecular ions (cationized or protonated) of oligomers were observed, with no evidence of fragmentation or field-enhanced reaction. Significantly, the extremely close agreement between molecular weight averages calculated from EH mass spectra and values obtained by conventional methods indicated that sampling efficiencies were similar for structurally similar ions, regardless of mass or charge.

The work described here tests the applicability of EHMS as a probe of complex lability. Specifically, the method has been used to characterize bipyridyl (bpy) complexes of ruthenium(II) and chromium(II) in glycerol. Tris(bipyridyl)ruthenium(II) complex ($Ru(bpy)_3^{2+}$) has been the topic of extensive study because of its increasingly important role in the study of electron-transfer reactions mimicking photosynthesis.[18] This complex does not undergo significant ligand exchange in solution and should have a simple and predictable mass spectrum, unless the sampling process induces fragmentation or other molecular transformation.

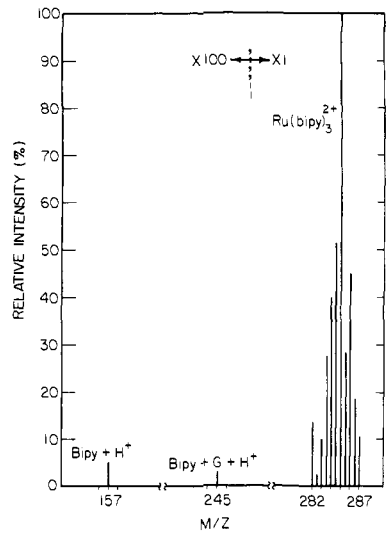

Figure 1. Positive-ion EH mass spectrum of $Ru(bpy)_3Cl_2$ (0.1 mol %) with NaCl (5.0 mol %) in glycerol (100.0 mol %).

By contrast, chromium(II) complexes are relatively labile. A solution of $Cr(bpy)_3^{2+}$ in the presence of another ligand (such as Cl^-) would be expected to contain a mixture of ligand-exchange products. Determination of these products would provide valuable evidence of their relative stabilities. Thus, these two compounds should provide excellent tests of the utility of EHMS as a probe of the solution chemistry of transition metal complexes.

Experimental Section

Mass spectra were obtained with a double-focusing mass spectrometer (AEI MS902) equipped with an EH ion source described elsewhere.[12,14] Source emitter potential was about ±8.5 kV; extractor potential was roughly ∓1.5 kV; the collector was fixed at ground potential. For all spectra, exact emitter potential and spectrometer electric sector potential were empirically matched; thus only ions that had not undergone any metastable evaporative loss of solvating glycerol molecules prior to the electric sector were detected.[17] Spectrometer resolution of about 600 was employed. At this resolution, the sensitivity was 10^{-13} to 10^{-14} C/μg.[16] Typical ion emission current was 10^{-5} to 10^{-6} A; ion current passing through the electric sector was typically on the order of 10^{-10} A. The electron multiplier voltage was set between −2 and −4 kV, giving a gain of roughly 10^5. Sample consumption was on the order of a few microliters per hour.

$Cr(bpy)_3(ClO_4)_2$ was synthesized from bipyridine (Aldrich) and $CrCl_3$ (Baker) or $Cr(TFA)_3$ (TFA = trifluoroacetate) following the procedure outlined in ref 19. $Cr(TFA)_3$ was prepared by heating a mixture of $K_2Cr_2O_7$ (Fisher) and trifluoroacetic acid (Aldrich) in absolute ethanol (U.S. Industries) to dryness. $Zn(bpy)_3(ClO_4)_2$ was a byproduct of the synthesis of the chromium complex. $Ru(bpy)_3Cl_2$ (G. F. Smith), NaCl (Mallinckrodt), and glycerol (Fisher) were used as received.

Glycerol solutions of $Ru(bpy)_3Cl_2$, $Cr(bpy)_3(ClO_4)_2$, and $Zn(bpy)_3(ClO_4)_2$ (all ~0.1 mol %) with NaCl (~5.0 mol %) as supporting electrolyte were prepared by dissolving the complexes and salt with heating (~60 °C) and vigorous stirring for 15 min. All solutions were degassed[12,14] to $\lesssim 1 \times 10^{-2}$ torr (overnight) before EHMS analysis. Positive and negative ion spectra were obtained. However, negative ion spectra contained only ions attributable to Cl^-, ClO_4^-, and their glycerol solvation products. Because no negative ions of analytical interest were observed, the negative ion spectra are not included in the discussion below.

Results and Discussion

Initial studies involved $Ru(bpy)_3Cl_2$ in glycerol solution with NaCl. Ions of NaCl supporting electrolyte were observed as in earlier studies.[9,12-17] These "background" ions (Na^+ and its glycerol solvated adducts) have been removed from the figures for clarity.

The only ruthenium complex ion detected was $Ru(bpy)_3^{2+}$ (fw = 570; mass to charge ratio, m/z 285) (Figure 1). No chlororuthenium complex nor solvated ruthenium complex was detected.

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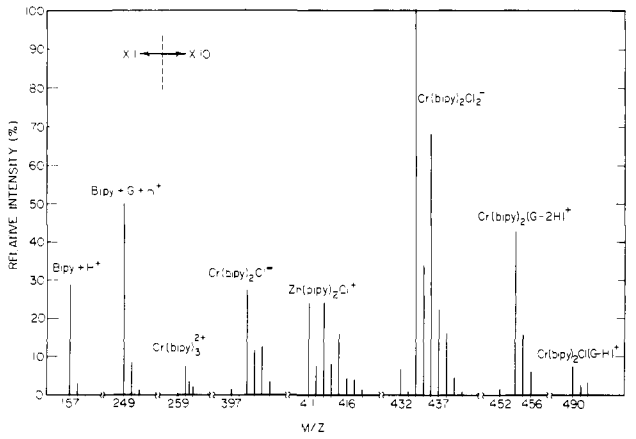

Figure 2. Positive-ion EH mass spectrum of $Cr(bpy)_3(ClO_4)_2$ (0.1 mol %, prepared from $CrCl_3$) with NaCl (5.0 mol %) in glycerol (100.0 mol %).

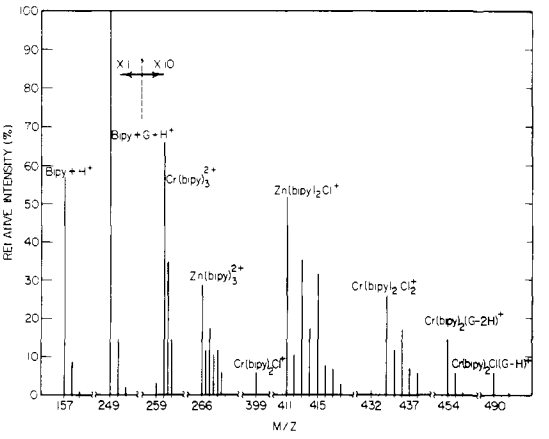

Figure 3. Positive-ion EH mass spectrum of $Cr(bpy)_3(ClO_4)_2$ (0.1 mol %, prepared from $Cr(TFA)_3$) with NaCl (5.0 mol %) in glycerol (100.0 mol %).

Thus, as expected, no ligand exchange between the $Ru(bpy)_3^{2+}$ complex and Cl^- or solvent occurred.

The ruthenium complex cation was identified by its m/z and the abundance of natural isotopes. Ruthenium isotopes of several atomic weights have significant natural abundances. Measured intensities of ions in the cluster assigned to $Ru(bpy)_3^{2+}$ matched very well with theoretical values calculated from known abundances of ruthenium isotopes (contributions from ^{13}C were also included).

Besides the ruthenium complex ion, a small amount of protonated bipyridine was also detected in the ruthenium sample ($[bpy + H]^+$, m/z 157). Some of these ions retained a solvent molecule ($[bpy + H + G]^+$ where G = glycerol, m/z 249). These bipyridyl ions had very low relative intensities (less than 0.05% of that due to the parent complex ion at m/z 285). No evidence of fragmentation or any other reaction promoted by the sampling electrostatic field was observed.

In contrast with the ruthenium sample, there was a large quantity of protonated bipyridine detected in the positive ion spectrum of the $Cr(bpy)_3(ClO_4)_2$/NaCl sample (Figure 2). As with the ruthenium sample, some of the protonated bipyridine retained a solvent molecule. More significantly, a mixture of chromium complexes was detected: $Cr^{III}(bpy)_2Cl(G-H)^+$ (A, m/z 490), $Cr^{III}(bpy)_2(G-2H)^+$ (B, m/z 454), $Cr^{III}(bpy)_2Cl_2^+$ (C, m/z 434), $Cr^{II}(bpy)_2Cl^+$ (D, m/z 399), and $Cr^{II}(bpy)_3^{2+}$ (E, m/z 260). Again, isotopic clusters provided confirmation of the identity of the metal and the number of chlorine atoms in each ion except for A and E, which were present at levels too low (~5%) for precise determination of experimental isotope abundances. The observation of these mixed ligand complexes and the large quantity of bipyridine suggested that $Cr(bpy)_3^{2+}$ underwent ligand exchange with Cl^- (ions A, C, and D) and solvent (ions A and B). To test whether ligand exchange between bipyridine and chloride had taken place after dissolving the complex and NaCl in glycerol, or if the synthesis procedure had prepared a series of mixed ligand complexes, chromium(III) trifluoroacetate was used to replace $CrCl_3$ as starting material in the synthesis of the chromium(II)–bipyridine complex. A mixture of chlorobipyridylchromium complexes, similar to the initial sample, was detected from this newly prepared complex (Figure 3). Since this sample was not exposed to Cl^- during its synthesis, the chloro complexes detected had to originate from ligand-exchange reactions between $Cr(bpy)_3^{2+}$ and Cl^- in glycerol. Ions A and B also resulted from ligand exchange in glycerol. In complex A, the glycerate anion, $(G-H)^-$, occupied one coordination site, whereas in complex B, the glycerate dianion, $(G-2H)^{2-}$, acted as a bidentate ligand.

The most abundant complex ions observed in Figure 2 were B and C, chromium(III) complexes. These were presumably formed by air oxidation of the Cr(II) complexes. Cr(III) complexes are kinetically inert to ligand exchange. Thus, after these complexes were formed, they would not exchange their ligands with the surrounding species, but should accumulate in solution.

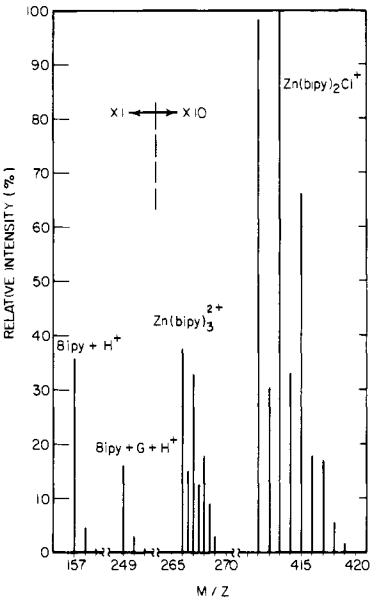

Figure 4. Positive-ion EH mass spectrum of $Zn(bpy)_3(ClO_4)_2$ (0.1 mol %) with NaCl (5.0 mol %) in glycerol (100.0 mol %).

In Figure 3, E, a chromium(II) complex, was observed to be more abundant than B and C. This spectrum was obtained from a sample for which particular care was taken during sample preparation and loading to minimize the exposure of the analyte solution to air. When this analyte solution was subsequently left standing in air overnight, the relative abundance of E to B and C approached that of Figure 2 for which air oxidation was not avoided from the outset.

Also detected in both chromium samples was an ion with base peak of m/z 411 (Figures 2 and 3). The ion was assigned the structure $Zn(bpy)_2Cl^+$, confirmed by its isotopic pattern. This ion matched very well with the major ion observed in the positive ion spectrum of $Zn(bpy)_3(ClO_4)_2$ with NaCl as supporting electrolyte (Figure 4). The presence of Zn was confirmed by X-ray analysis. The detection of zinc impurity in the chromium complex was not surprising because zinc metal was used as a reductant in preparing the chromium complex. Clearly, some of the Zn^{2+} produced during chromium reduction was complexed upon the addition of bipyridine and subsequently coprecipitated with the perchlorate salt of the chromium complex.

Thus, all ions detected in the EH mass spectra of labile chromium complexes can be reasonably explained as products of conventional solution phase complexation chemistry. Results here, as with the ruthenium complex and all previous EHMS studies, give no evidence of fragmentation or other field-induced chemistry. While quantitative aspects here are not as readily subject to test as they were in some previous studies (especially that with

poly(ethylene glycols)[16]), the similarity of general ion structures and the intensity changes resulting from air oxidation of the sample prepared from $Cr(TFA)_3$ suggest that spectra provide at least semiquantitative measures of the relative abundances of ions in the solutions. Extensive studies are currently under way, with an aim of better quantitation through a more detailed understanding of the EH ionization process.

Conclusions

The results of this study suggest that EHMS can provide a simple and direct probe for characterization of the solution chemistry of transition metal complexes. The spectra accurately reflect the relative lability of the metal complexes sampled; that is, the labile chromium(II) complex undergoes ligand exchange reactions whereas the inert ruthenium(II) complex does not. Furthermore, because of the sensitivity of mass spectrometry, impurities in solution can also be detected and identified.

The need for low volatility and high electrical conductivity for solutions sampled with existing EH instrumentation enforce some constraints on the range of systems which can be sampled. While the latter condition (conductivity) is readily met in solutions of transition metal complexes, the former (volatility) precludes the use of many important solvents (most notably, water). Design refinements presently under consideration may relieve volatility restrictions. However, even in its present form, EHMS appears to be a valuable probe of these (and related) systems.

Acknowledgment. The authors gratefully acknowledge Dr. L. R. Faulkner and Mr. T. Emilsson for their helpful discussions and for providing the ruthenium, chromium, and zinc complexes. This research was supported by the National Institutes of Health (Grant GM 19749) and the National Science Foundation (Grant DMR-80-24632 jointly funded by the Army Research Office). The Materials Research Laboratory is supported in part by the National Science Foundation (Grant DMR-80-20250).

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Cr(bpy)_3^{2+}$, 17632-84-7; $Cr(bpy)_2Cl^+$, 82621-23-6; $Cr(bpy)_2Cl_2^+$, 21748-31-2; $Cr(bpy)_2(G\text{-}2H)^+$, 82621-24-7; $Cr(bpy)_2Cl(G\text{-}H)^+$, 82621-25-8.

Rotation about the Carbonyl Carbon–Nitrogen Bond in Micelles of *N*-(Dodecyloxycarbonyl)sarcosinate

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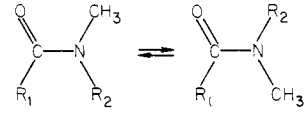
Abstract: The sodium salt of the title compound forms micelles readily, exhibiting a critical micelle concentration of 6×10^{-4} M at 25 °C. Quasi-elastic light scattering shows that most of the micelles are approximately 6.0 nm in diameter, although indications of larger aggregates (~170 nm diameter) were also observed. These diameters do not change beyond experimental error over the temperature range 25–50 °C. Proton NMR experiments were used to determine the kinetics of rotation about the carbonyl carbon–nitrogen bond of the detergent both in micelles and in the monomer. While $\Delta G^{\ddagger}$ for rotation was found to be independent of aggregation state, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the process are substantially larger in the micelle. Variations in the activation parameters as the identity of the counterion is changed suggest that disruption of ionic interactions at the surface of the micelle is a part of the rotational process.

The nature of the micellar structures formed when amphiphilic molecules are placed in water has generated interest and controversy for many years.[1-3] At this point it seems to be generally accepted that these structures include a hydrophobic core region from which water is largely absent; outside this nucleus some fraction of the remaining hydrocarbon and the polar head group of each detergent are in contact with water to some degree. Many experiments point to decreased fluidity inside the micelle,[3,4] and carbon-13 NMR data suggest that molecular motion in the head-group region of these structures is significantly reduced in the micelle relative to that observed in nonmicellized states.[5] A fluidity gradient is observed as one progresses from the head-group region to the hydrophobic core with motion becoming freer as the core is approached. These conclusions are similar to observations made with lipid bilayers and biological membranes—in these systems the polar surface is highly ordered, and molecular motion increases in rate and amplitude as the more hydrophobic interior of the structure is approached.[6]

Many micelles formed by ionic amphiphiles in water appear to be approximately spherical structures coated with electrical charges, first those of the ionic groups of the detergent and then a layer containing a large fraction of the counterions that accompanied the detergent into solution. A highly heterogeneous electrical environment is thus present at the "surface" of a micelle that is not unlike that which exists on the surface of a cell membrane.

There is evidence that the relative conformational energies of the two forms of the amide functional group (Ia, Ib) are altered



Ia Ib

when this group is present at the surface of a micelle,[7] and when surfactant molecules incorporating this structural element form micelles, the population of the trans isomer (Ib) relative to the

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