Electrospray Mass Spectrometric Detection of Neutral Rhenium Bipyridine Complexes Using $NaNO_3$ as an Ionization Agent

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Sodium nitrate can be used as a chemical ionization agent in the electrospray mass spectrometric analysis of neutral rhenium bipyridine complexes.

In recent years electrospray (ES) mass spectrometry for metal complexes has received a great deal of attention because it is useful for measuring the molecular masses of unstable species such as reaction intermediates.[1] For example, Arakawa *et al.* elucidated the photosubstitution of ruthenium complexes,[2] and we also very recently examined the intermediates of CO_2 photofixation caused by the rhenium complex.[3] Although this technique is quite useful for such purposes, its application is virtually restricted to charged species in solution.[1-6] To detect neutral species, Henderson *et al.* have shown that the addition of silver(I) and alkoxide (OR^-) ions to solutions containing neutral metal carbonyl complexes produce ES active species, i.e., [complex + Ag]$^+$ and [complex + OR]$^-$, respectively.[4,5] However, these ionization agents have a tendency to linger in the ES mass spectrometer (metallic silver may deposit on the ES probe) and sometimes cause undesired redox reactions or ligand substitutions of active samples. Therefore, milder ionization agents are required.

Here, we report that the addition of $NaNO_3$ can be used to promote the ionization of neutral rhenium bipyridine complexes which have no charge, [*fac*-Re(X_2bpy)$(CO)_3$Y] (X_2bpy = 4,4'-X_2-2,2'-bipyridine; X = H, Me, CF_3; Y = CN, Cl, Br, OCHO, OH). These complexes are attractive in view of their CO_2 reduction photocatalysis.[7,8]

The positive ion ES mass spectra of these complexes dissolved in methanol showed no species including the [Re(X_2bpy)$(CO)_3$Y] moiety.[9] Namely, they showed no peaks or showed peaks corresponding to fragment ions such as [Re(X_2bpy)$(CO)_3$]$^+$. However, the addition of a small quantity of $NaNO_3$ showed the appearance of peaks corresponding to Na^+ adducts [Re(X_2bpy)$(CO)_3$Y + Na]$^+$.[10,11]

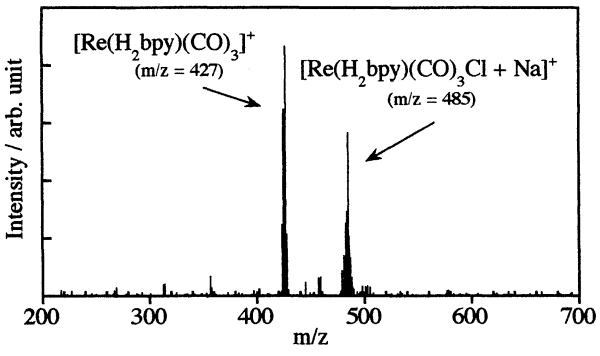

Figure 1. Electrospray mass spectrum of Re(H_2bpy)$(CO)_3$Cl containing $NaNO_3$. Drift voltage is 40 V.

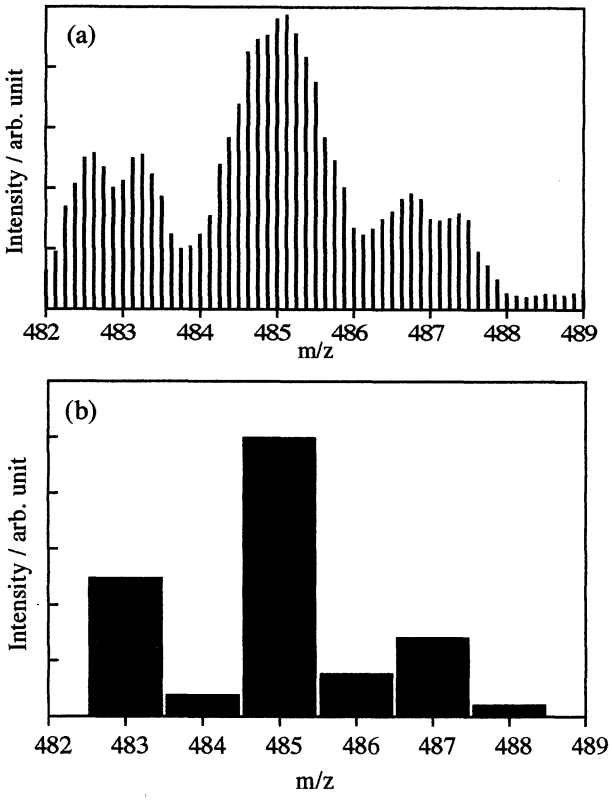

Figure 2. Isotope distribution for the peak corresponding to [Re(H_2bpy)$(CO)_3$Cl + Na]$^+$: (a) observed and (b) calculated.

Figure 1 shows a typical spectrum of Re(H_2bpy)$(CO)_3$Cl containing $NaNO_3$. The peak assigned to [Re(H_2bpy)$(CO)_3$Cl + Na]$^+$ (m/z = 485) was clearly detected and the observed isotope distribution pattern was in good agreement with that of the calculated one (Figure 2).

All the complexes listed in Table 1 caused the peaks assigned to the Na^+ adducts. However, in the case of Re(H_2bpy)$(CO)_3$OH, a dominant peak for a methoxy complex [Re(H_2bpy)$(CO)_3OCH_3$ + Na]$^+$ (m/z = 481) was detected instead of [Re(H_2bpy)$(CO)_3$OH + Na]$^+$, indicating that the OH ligand is substituted by OCH_3 from methanol.

When the complexes were dissolved in *N,N*-dimethylformamide (DMF) instead of methanol, the addition of $NaNO_3$ was not useful in detecting the complexes as Na^+ adducts because Na^+ ions preferentially react with DMF to produce [DMF + Na]$^+$ (m/z = 96) and [2DMF + Na]$^+$ (m/z = 169). Therefore, the selection of the solvent is important in this ionization method.

In contrast to these complexes, the rhenium complexes having no bipyridine ligand, e.g., Re$(CO)_5$Cl, did not cause any Na^+

Table 1. Electrospray mass spectral data for rhenium bipyridine complexes containing $NaNO_3$

$Re(X_2bpy)(CO)_3Y$ X	Y	Drift voltage / V	Detected ions derived from the complexes (m/z) [a]
H	CN	10-20	$[Re(H_2bpy)(CO)_3CN+Na]^+$ (476)
		40-60	$[Re(H_2bpy)(CO)_3CN+Na]^+$ (476), $[Re(H_2bpy)(CO)_2CN+Na]^+$ (448)
H	Cl	10-60	$[Re(H_2bpy)(CO)_3Cl+Na]^+$ (485), $[Re(H_2bpy)(CO)_3]^+$ (427)
H	Br	10-60	$[Re(H_2bpy)(CO)_3Br+Na]^+$ (529), $[Re(H_2bpy)(CO)_3]^+$ (427)
H	OCHO	10-60	$[Re(H_2bpy)(CO)_3OCHO+Na]^+$ (495), $[Re(H_2bpy)(CO)_3]^+$ (427)
H	OH	10	$[Re(H_2bpy)(CO)_3OMe+Na]^+$ (481), $[Re(H_2bpy)(CO)_3]^+$ (427)
Me	Cl	10-60	$[Re(Me_2bpy)(CO)_3Cl+Na]^+$ (513), $[Re(Me_2bpy)(CO)_3]^+$ (455)
CF_3	Cl	10-60	$[Re\{(CF_3)_2bpy\}(CO)_3Cl+Na]^+$ (621), $[Re\{(CF_3)_2bpy\}(CO)_3]^+$ (563)

[a] Species are identified by the peak of greatest intensity in the isotope distribution pattern.

adducts by an addition of $NaNO_3$. This finding suggests that the Na^+ ion interacts with the bpy ligand on the rhenium complexes.

Further application of this ionization method to a wide range of complexes and the effect of the solvent are being investigated in our laboratory.

References and Notes

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9 Positive ion ES mass spectra were recorded on a Hitachi M-1200 mass spectrometer with a M-1206 ES probe. The needle voltage was 3 kV. A Hitachi L-6200 pump was used to deliver the samples to the ES probe with a flow rate of 0.05 ml min^{-1}. The mobile phase was methanol. The methanol solution of each complex (2 mmol dm^{-3}, 1 μl) was introduced into the ES probe through a Rheodyne 7125 injector.

10 To the methanol solution of each complex was added the same volume of methanol solution of $NaNO_3$ (1 mmol dm^{-3}) and then introduced into the ES probe.

11 Sodium nitrate is preferred as the Na^+ source, because NO_3^- ion causes no ligand substitution of the samples. Sodium acetate was also effective for this ionization.