# Gas-Phase Reactivity of Coordinatively Unsaturated Transition Metal Complex Ions toward Molecular Oxygen

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Electrospray mass spectrometry is used to investigate the reactivity of the coordinatively unsaturated ions $[M(bipy)_2]^{2+}$ (M = Cr, Ru, Os) and $[M(bipy)]^+$ (M = Co, Ni) toward $O_2$ to give the dioxygen adducts $[M(bipy)_2O_2]^{2+}$ (M = Cr, Ru, Os) and $[M(bipy)O_2]^+$ (M = Co, Ni). CID experiments with the $[M(bipy)_2O_2]^{2+}$ and $[M(bipy)O_2]^+$ adducts show that the loss of a mass equivalent to two oxygen atoms is the predominant process for $[M(bipy)_2O_2]^{2+}$ (M = Cr, Ru) and $[M(bipy)O_2]^+$ (M = Ni, Co). In contrast, weak signals assigned to $[Os(bipy)O_2]^+$, $[Os(bipy)O_2]^{2+}$, and $bipy^{+\bullet}$ indicate loss of a bipyridine ligand from $[Os(bipy)_2O_2]^{2+}$ rather than $O_2$ loss. This result may have structural implications and a dioxo Os(VI) complex cation, $[Os(bipy)_2(O)_2]^{2+}$, is proposed for the Os−dioxygen adduct. This assignment is consistent with the known solution and solid-state chemistry of osmium. Formation of $[Os^{VI}(bipy)_2(O)_2]^{2+}$ involves a formal oxidation of the Os(II) to an Os(VI) and concomitant $O_2$ four-electron reduction of $O_2$. Even though loss of $O_2$ rather than bipy was the predominant process observed in CID experiments for the Ru adduct, a structural formulation of an analogous dioxo species is not excluded for $[Ru(bipy)_2O_2]^{2+}$.

## Introduction

Some of the first coordination complexes to be examined by ESIMS were the tris(bipyridine) complexes.[1] Depending on the source conditions, these complexes can lose one or two of the bipyridine ligands, leaving a coordinatively unsaturated transition metal ion.[2] In the present study, we have examined the ability of such ions to undergo ion−molecule reactions (IMRs) with molecular oxygen. The study of reactions of coordinatively unsaturated transition metal ions with dioxygen is useful since such processes are often essential in the activation of molecular oxygen for its subsequent utilization in oxidation reactions in biological and other systems. The four-electron conversion of dioxygen to oxide (or water/hydroxide) ligands, and the reverse of this process, is a subject under considerable debate in the field of bioinorganic chemistry, due to metalloenzyme involvent in dioxygen-utilizing and -generating processes.[3] Studies of molecular activation under well-controlled conditions can contribute to the elucidation of the mechanisms of molecular oxygen activation.

Gas-phase ion−molecule reactions (IMRs) of molecular oxygen with metal-containing ions have been studied earlier for singly charged metal and metal cluster (e.g. $Fe_n^+$) ions by Schwarz and co-workers.[4] As well, singly charged metal oxide ions have been generated by O atom transfer from $O_2$, $N_2O$, and $CO_2$ to bare metal/metal cluster ions.[5] In these studies the ions are produced by laser ablation of metal surfaces or by collision-induced dissociation (CID) of singly charged carbonyl complexes. Such methods give only low yields of doubly charged ions, and consequently their gas-phase chemistry has been much less studied.[6] With electrospray ionization mass spectrometry (ESIMS) strong currents of multiply charged transition metal complex ions can be generated, and their reactivity, e.g. in IMRs and under photoactivation, can be studied.[7,8]

## Experimental Section

Spectra were recorded using a Finnigan TSQ 700 triple-quadrupole mass spectrometer equipped with an atmospheric pressure ionization (API) source and operating in the electrospray mode. The source in this instrument is constructed with a heated capillary (150 °C) before the skimmer and an octapole which functions as a focusing device between the skimmer and the first mass filter. The spray was generated with a microelectrospray probe with a flow of 0.4 $\mu$L/min and a spray potential of 3.9−4.0 kV. The coordinatively unsaturated complexes were generated by CID in the skimmer region by changing the potentials of the tube lens or the source octapole (source CID). The $[M(bipy)_2]^{2+}$ and $[M(bipy)]^+$ complexes generated were allowed to react with dioxygen (ca. 3 mTorr) (multiple-collision conditions) in the collision

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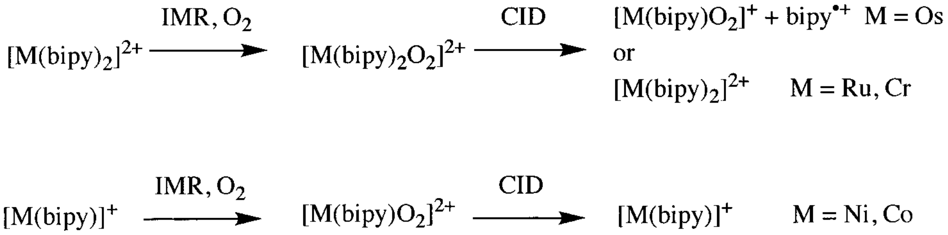
**Scheme 1**[a]



$$[M(bipy)_2]^{2+} \xrightarrow{IMR,\ O_2} [M(bipy)_2O_2]^{2+} \xrightarrow{CID} [M(bipy)O_2]^+ + bipy^{\bullet+} \quad M = Os \quad \text{or} \quad [M(bipy)_2]^{2+} \quad M = Ru, Cr$$

$$[M(bipy)]^+ \xrightarrow{IMR,\ O_2} [M(bipy)O_2]^{2+} \xrightarrow{CID} [M(bipy)]^+ \quad M = Ni, Co$$

[a] IMR = ion−molecule reaction; CID = collision-induced dissociation.

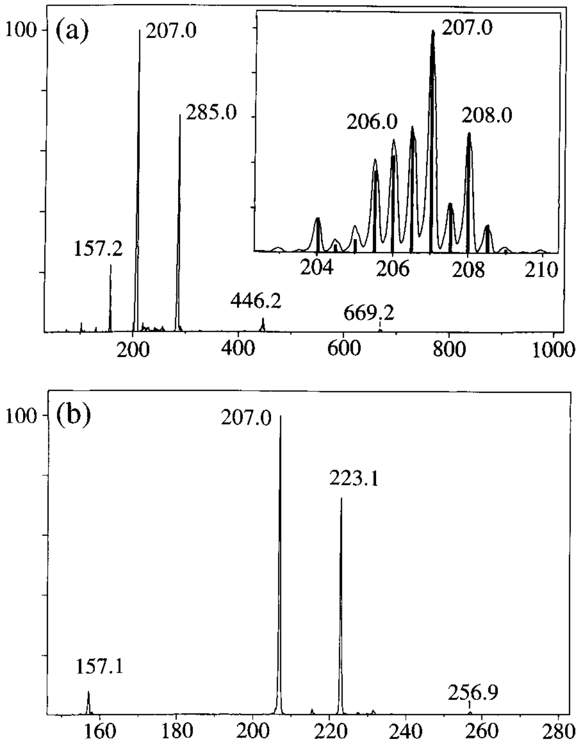


**Figure 1.** (a) Mass spectrum obtained for the source CID of $[Ru(bipy)_3]^{2+}$ (*m*/*z* 285.0). The inset shows an expansion of the peak assigned to the $[Ru(bipy)_2]^{2+}$ ion (*m*/*z* 207.0); the calculated fit is drawn as bars (tube lens potential 80 V; source octopole potential −22.9 V). (b) Ion−molecule reaction of $[^{102}Ru(bipy)_3]^{2+}$ (*m*/*z* 207.0) with $O_2$ to give $[^{102}Ru(bipy)_2O_2]^{2+}$ (*m*/*z* 223.1) ($P_{O_2}$ ca. 3 mTorr in the collision cell with an offset of −23.4 V corresponding to an *E*(lab) of 1.0 eV).

cell with an *E*(lab) of 1.0 eV, for the doubly charged ions. CID experiments with the $[M(bipy)_2O_2]^{2+}$ and $[M(bipy)O_2]^+$ ions were carried out by changing the offset of the collision cell from −3 V to approximately −100 V, depending on the particular dioxygen adduct, and using 0.10−0.14 mTorr of 99.99% argon (single-collision conditions) as the collision gas.

## Results and Discussion

Scheme 1 summarizes the reactions carried out with coordinatively unsaturated metal−bipy ions and the ionic products detected after reaction with dioxygen. CID experiments have been carried out on the dioxygen adducts and provide some clues to their possible structural formulations.

The $[M(bipy)_2]^{2+}$ and $[M(bipy)]^+$ ions were generated in the source by increasing the potential in the skimmer region or by decreasing the potential in the source octapole. The reactivity of these ions toward dioxygen was tested in the collision octapole; multiple-collision conditions were used while the velocity of the ions was kept very low in order to optimize the number of reactive collisions. The interpretations of the spectra were confirmed through reactions with $^{18}O$-labeled molecular oxygen, by conducting the experiment with two different isotopomers of the reagent ion where possible and by checking that the abundance of the dioxygen adducts increased with the oxygen pressure in the collision octapole.[9]

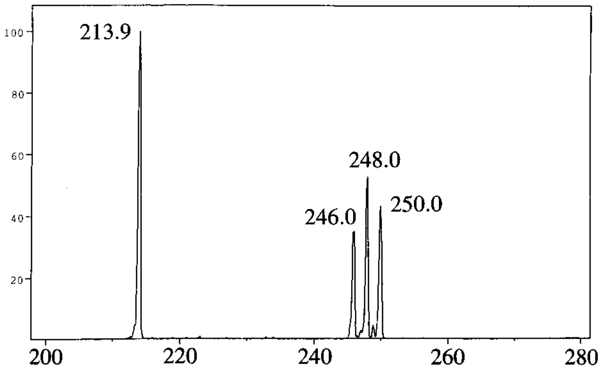


**Figure 2.** Ion−molecule reaction of $[^{58}Ni(bipy)]^+$ (*m*/*z* 213.9) with labeled dioxygen with an approximate isotopic mixture of 50% $^{18}O$ and 50% $^{16}O$, to give $[Ni(bipy)^{16}O_2]^+$, $[Ni(bipy)^{16}O^{18}O]^+$, and $[Ni(bipy)^{18}O_2]^+$ at *m*/*z* 246.0, 248.0, and 250.0, respectively (tube lens potential 130 V; source octapole potential −3.0 V). The peak intensities correspond to those measured by EIMS for the labeled dioxygen mixture.

Reactions of the bis(bipyridine) ions $[M(bipy)_2]^{2+}$ with $O_2$ were investigated for M = Cr, Mn, Fe, Co, Ni, Cu, Ru, and Os. For the complexes with M = Cr, Ru, and Os, product ions assignable to the dioxygen adducts, $[M(bipy)_2O_2]^{2+}$, were observed; the other precursors did not yield detectable product ions under the conditions used. The observed reactivity of this series of coordinatively unsaturated complex cations toward dioxygen correlates well with the propensity of Cr, Ru, and Os for attaining the high oxidation states known from solution and solid-state chemistry. Typical results are illustrated in Figure 1 by data from the Ru series. The source CID spectrum of $[Ru(bipy)_3]^{2+}$ is shown in Figure 1a. The spectrum obtained when $[^{102}Ru(bipy)_2]^{2+}$ reacts with molecular oxygen to give $[^{102}Ru(bipy)_2O_2]^{2+}$ is shown in Figure 1b. Selection of the $^{104}Ru$-containing isotopomer gave the expected shift of the product ion from *m*/*z* 223 to *m*/*z* 224.

The reaction of mono(bipyridine) complex ions, $[M(bipy)]^+$, with dioxygen were examined for M = Ni, Co, and Cu since only ions of this composition were detected with these particular metals. Only the Ni- and Co-containing complex ions gave detectable dioxygen adducts with the composition $[M(bipy)O_2]^+$. Figure 2 shows the spectrum obtained for the ion−molecule reaction of $[Ni(bipy)]^+$ with $^{18}O$-enriched $O_2$.

The composition of the $[M(bipy)_2O_2]^{2+}$ and $[M(bipy)O_2]^+$ ions are unequivocal, but their structures remain speculative. End-on and side-on binding modes are known for $O_2$. A formal “inner-sphere” electron transfer may occur, so that the dioxygen

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(9) Available as Supporting Information.

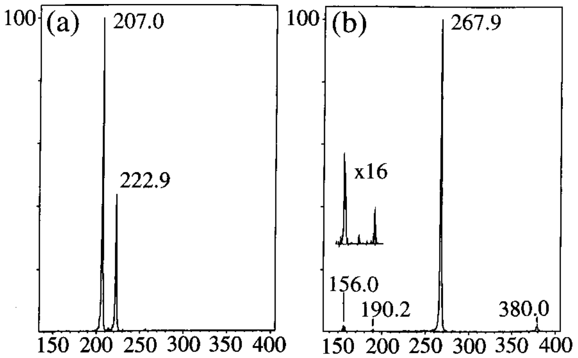

**Figure 3.** CID experiments with the Ru and Os dioxygen adduct ions: (a) collision energy 4.1 eV (center of mass), collision gas 0.12 mTorr of 99.99% Ar, precursor ion $[Ru(bipy)_2O_2]^{2+}$ (*m/z* 222.9), product ion $[Ru(bipy)_2]^{2+}$ (*m/z* 207.0); (b) collision energy 4.0 eV (center of mass), collision gas 0.12 mTorr of 99.99% Ar, precursor ion $[Os(bipy)_2O_2]^{2+}$ (*m/z* 267.9); the very weak signals at *m/z* 380.0, 190.2, and 156.0 are assigned to product ions $[Os(bipy)O_2]^+$, $[Os(bipy)O_2]^{2+}$, and $bipy^{+\bullet}$.

is formally reduced and the metal ion formally oxidized, possibly involving O−O bond rupture. We attempted to elucidate the bonding structures of the $[M(bipy)_2O_2]^{2+}$ and $[M(bipy)O_2]^+$ ions by subjecting them to CID in MS/MS/MS experiments: $[M(bipy)_2]^{2+}$ and $[M(bipy)]^+$ were generated in the skimmer region and allowed to react with oxygen in the source octapole. The adducts $[M(bipy)_2O_2]^{2+}$ and $[M(bipy)O_2]^+$ were subsequently subjected to collisional activation in the collision region. The resultant CID spectra of $[Ru(bipy)_2O_2]^{2+}$ and $[Os(bipy)_2O_2]^{2+}$ obtained in this way are shown in Figure 3. The loss of a mass equivalent to two oxygen atoms is the predominant process for $[M(bipy)_2O_2]^{2+}$ (M = Cr, Ru; Figure 3a) and $[M(bipy)O_2]^+$ (M = Ni, Co). These results contrast with those obtained for $[Os(bipy)_2O_2]^{2+}$ as the parent ion, for which no formation of $[Os(bipy)_2]^{2+}$ (expected at *m/z* 252) is observed (Figure 3b). Instead, weak signals assigned to $[Os(bipy)O_2]^+$, $[Os(bipy)O_2]^{2+}$, and $bipy^{+\bullet}$ indicate loss of a bipyridine ligand from $[Os(bipy)_2O_2]^{2+}$, either as a neutral molecule or as a radical cation, in preference to $O_2$. These results suggest that the dioxygen adduct, at least in the case of Os, is an "osmyl" type complex cation, e.g. $[Os(bipy)_2(O)_2]^{2+}$, in which the O−O bond of the dioxygen is broken and both oxygen atoms are independently bound to the Os atom. Thus a concomitant four-electron oxidation of the Os(II) atom, to give formally an Os(VI) atom, and a four-electron reduction of $O_2$ are implied. The $[Os^{VI}(bipy)_2O_2]^{2+}$ cation is known in the complex $[Os(bipy)_2O_2](ClO_4)_2$, which was prepared by oxidation of $Os^{II}(bipy)_2CO_3$ by Ce(IV) in aqueous solution;[10] i.e., the oxo ligands in the solid-state $[Os(bipy)_2O_2](ClO_4)_2$ are derived from water. Isoelectronic Ru and Os complexes show similar solution chemistry; thus we do not exclude an analogous dioxo structure, for $[Ru(bipy)_2O_2]^{2+}$ on the basis of the CID results, even though $O_2$ rather than bipy loss from the Ru-containing complex ions is apparent using similar CID conditions. The differences in fragmentation may be due to different kinetic barriers for the steps involved in these processes. Apart from some sort of gas-phase association between neutral $O_2$ and $[M(bipy)_2]^{2+}$, another alternative structural formulation for $[M(bipy)_2O_2]^{2+}$ (M = Cr, Ru) involves a two- or one-electron inner-sphere electron transfer to give a M(IV)−peroxo or a M(III)−superoxide complex ion; such species are particularly relevant to the solution and solid-state chemistry of chromium.[11]

**Concluding Remarks.** The results here demonstrate that ESIMS enables studies of the reactivity of coordinatively unsaturated transition metal complex ions toward $O_2$. The gaseous coordinatively unsaturated transition metal ions containing 2,2′-bipyridine ligands, $[M(bipy)_2]^{2+}$ and $[M(bipy)]^+$, react with molecular oxygen to give the dioxygen adducts $[M(bipy)_2O_2]^{2+}$ (M = Cr, Ru, Os) and $[M(bipy)O_2]^+$ (M = Co, Ni) and provide evidence for rupture of the O−O bonds in the Os adduct.

It is important to keep in mind that the internal energy distribution of ions in the gas phase is difficult to assess and electronically excited states may well be involved in the reaction mechanisms. To our knowledge, this study represents the first report of gas-phase reactions of $O_2$ with doubly charged coordinatively unsaturated coordination complex ions.

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**Supporting Information Available:** Spectra obtained from the reactions of $[Cr(bipy)_2]^{2+}$, $[Os(bipy)_2]^{2+}$, and $[Co(bipy)_2]^+$ with $O_2$ labeled with 50% $^{18}O$ (Figures S1−S3), the EI mass spectrum of the labeled dioxygen mixture (Figure S4), a graph showing the ratio of the intensities of the dioxygen adducts to the intensities of the presursor ions as a function of the pressure of dioxygen in the collision cell (Figure S5), CID spectra of $[Cr(bipy)_2O_2]^{2+}$, $[Ni(bipy)_2O_2]^+$, and $[Co(bipy)_2O_2]^+$ at 4 eV using 0.1 mTorr of argon (Figures S6−S8), and a comparison of the appearance curves ($E$(CM) = 0−10 eV) obtained for the fragmentation of the five dioxygen adducts (Figure S9) (12 pages). Ordering information is given on any current masthead page.

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