

Review

Gas-phase ion–molecule reactions of divalent metal complex ions: Toward coordination structure analysis by mass spectrometry and some intrinsic coordination chemistry along the way

M. Yajaira Combariza, Angela M. Fahey, Aleksandr Milshteyn, Richard W. Vachet*

Department of Chemistry, LGRT 701, 710 N. Pleasant St., University of Massachusetts at Amherst, MA 01003, USA

Received 20 April 2005; received in revised form 26 May 2005; accepted 31 May 2005

Available online 1 July 2005

Abstract

Gas-phase ion–molecule reactions of divalent metal complex ions are strongly affected by the coordination structure around the metal. This review describes how association reactions between reagent ligands and complex ions proceed to extents that depend upon a metal complex's coordination number, types of coordinating functional groups and coordination geometry. The coordination number of a metal complex affects its reactivity because complexes of divalent metal ions will add reagent molecule(s) to fill vacant coordination sites. The thermodynamics and kinetics of these reactions are very sensitive to both the types of functional groups bound to the metal and the geometry of the groups around the metal ion. Such a strong dependency on the coordination structure of a metal complex suggests that ion–molecule reactions might make mass spectrometry suitable for elucidating a metal's coordination structure. Given mass spectrometry's inherent sensitivity and the ability to carefully control reaction conditions in a mass spectrometer, ion–molecule reactions have the potential, both analytically and fundamentally, to provide greater insight into the chemistry of divalent metal complexes.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Ion–molecule reactions; Quadrupole ion trap mass spectrometer; Divalent metal ions; Metal complex; Coordination structure

Contents

1. Introduction	110
2. Experimental methods	110
3. Coordination structure	110
3.1. Coordination number	111
3.1.1. Reagent gas considerations	111
3.1.2. Ligand-donor groups	113
3.1.3. Metal center	114
3.1.4. Coordination number determination—summary	115
3.2. Types of coordinating functional groups	115
3.3. Reagent gas considerations	117
3.3.1. Coordinating functional group determination—summary	118
3.4. Coordination geometry	118
3.5. The effect of steric interactions	120
4. Concluding remarks	122
Acknowledgement	123
References	123

* Corresponding author. Tel.: +1 413 545 2733; fax: +1 413 545 4490.

E-mail address: rwwachet@chem.umass.edu (R.W. Vachet).

1. Introduction

It is axiomatic in chemistry that “structure controls function.” For transition metal complexes, the function of interest is usually reactivity, and the structure that controls reactivity is coordination structure, which refers to the number, type and orientation of the ligand-donor groups around the metal center. A key role of this coordination structure is to tune the metal’s electronic structure and by doing so mediate any bond making and bond breaking. Ligand structure around the metal can also influence chemistry via steric control.

The relationship between a metal complex’s coordination structure and its chemical properties has led to the development of numerous spectroscopic techniques that can provide this structural information. These techniques include ground-state methods that use magnetic fields, valence excited-state methods that rely on UV or visible radiation and core excited-state methods based on X-ray radiation. This array of techniques has been developed because no one method provides all the desired information or is suitable for the analysis of every given complex. Special cases still arise in which traditional methods are unsuitable. One situation in which current methods often fail is when the complex of interest is present at very low concentrations. Under such conditions, most established techniques are unable to provide adequate signal for gathering the information of interest.

Because we are interested in studying the coordination structure of metal complexes present at trace levels in marine environments, we have begun to explore new ways to gather this information using mass spectrometry (MS). MS has in many ways revolutionized the analysis of peptides and proteins because of its ability to provide structural information while maintaining its exquisite sensitivity. A question that we have recently pursued is whether MS can similarly provide detailed structural information for metal complexes while maintaining this sensitivity. For organic ions structural information is typically obtained using a variety of dissociation techniques, including most often collision-induced dissociation (CID). For divalent metal–ligand complexes, structural information is often more difficult to obtain unambiguously using analytical CID [1–8] as it is performed during routine tandem MS (MS/MS) experiments on non-specialized mass spectrometers. Metal–ligand interactions are typically weaker than the covalent bonds in organic molecules, so collisional activation of metal complex ions can lead to the rearrangement of the metal center, resulting in dissociation chemistry that does not necessarily reflect the coordination environment of the metal. Furthermore, while the dissociation chemistry of a metal complex ion may still reflect its coordination structure in many cases, the relationship between the two is not always obvious. On the contrary, for small monovalent metal–ligand complexes, threshold CID measurements can provide very detailed thermodynamic information, and when combined with theoretical calculations, these measurements can also provide detailed structural insight [9–12]. Currently, though, threshold CID measurements are limited to

monovalent metal ions, but applications of these methods to divalent metal ions will undoubtedly appear in the future [13].

An alternate approach to gather insight into divalent metal coordination structure is reaction of metal complex ions with neutral reagents at thermal energies. These thermal reactions are much less likely than dissociation-based techniques to disrupt an ion’s structure, and these reactions usually generate product ion spectra that are much simpler to interpret. In addition, numerous potential reagents offer a broad scope of chemical reactions from which a complex’s structure may be deciphered. The use of such ion–molecule (I–M) reaction chemistry relies on the idea that just as a complex’s coordination structure affects its reactivity, so should a complex’s reactivity reflect its coordination structure. This review will demonstrate ways in which our group has used gas-phase I–M reactions to provide varying degrees of detail about a divalent metal complex’s coordination structure by choosing the appropriate reagent and collecting the proper experimental data. Furthermore, because these reactions are done in the gas-phase, some intrinsic coordination chemistry can be gathered at the same time. Of course, metal–ligand coordination chemistry is a very mature field, but studying the chemistry of divalent metal complexes without interferences from solvent or counterions can, in the very least, provide confirmation of well-developed theories (e.g. ligand field theory) especially for coordinatively unsaturated complexes. In other cases, new insight into divalent metal complex chemistry can be gathered.

2. Experimental methods

All of the experiments described in this review were performed on a modified Bruker Esquire-LC quadrupole ion trap mass spectrometer (QITMS). The instrumental modifications and the details of how the QITMS is used have been described elsewhere [14]. Briefly, metal complex ions are generated by electrospray ionization from solutions containing the complex of interest, and the ions are transferred via ion optics into the trapping volume of the QITMS. Ions of interest are then isolated in the gas-phase using supplementary waveforms applied to the endcap electrodes of the QITMS and allowed to react with neutral reagent gas(es) that are introduced into the vacuum system via a custom leak-valve system. Reaction times with reagent gases can range from 10 to 10,000 ms. The product ions formed from these reactions are then detected in a mass-selective manner by steadily increasing the rf voltage applied to the ring electrode while simultaneously applying a resonance ejection signal to the exit endcap electrode to enhance ion ejection to an electron multiplier.

3. Coordination structure

In the context of this review, coordination structure refers to the number, type and orientation of the ligands around a

Download English Version:

<https://daneshyari.com/en/article/9746642>

Download Persian Version:

<https://daneshyari.com/article/9746642>

[Daneshyari.com](https://daneshyari.com)