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Mass Spectra of Nickel Complexes measured by Liquid Ionization Mass Spectrometry

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(Received December 30, 1983)

Nickel halide complexes containing ethylenediamines as ligands were examined by liquid ionization mass spectrometry. Protonated molecules obtained as the base peaks and their isotope ratios agreed with their natural abundances. The mass spectra corresponding well to the structure of the complexes were better than their FD and FAB spectra.

1. Introduction

Application of electron ionization (EI) mass spectrometry to analysis of metal complexes has been limited to volatile compounds such as acetyl acetonates. Recently secondary ion mass spectrometry (SIMS),¹⁾ field desorption (FD),²⁻⁴⁾ fast atom bombardment (FAB)⁵⁻⁷⁾ and laser desorption method⁸⁾ have been successfully applied to several involatile transition-metal complexes. In general, however, FD, SIMS, and FAB spectra of the metal complex $[\text{Met}(\text{L})_m]\text{X}_n$ show monocationic metal complex ions $[\text{Met}(\text{L})_m]\text{X}_{n-1}^+$ but few intact molecular ions (M^+) or protonated

molecules (MH^+). That is the case for FD and SIMS spectra of Co complexes containing ethylenediamines as ligands.^{1,2)} Besides, mass spectra of nickel complexes containing ethylenediamines have not been reported.

We have developed a method which we call liquid ionization mass spectrometry (LI)^{9,10)} for analyzing organic compounds as a liquid at atmospheric pressure and reported that the method is useful for nonvolatile and thermolabile compounds.¹¹⁾ This paper describes LI mass spectra of nickel complexes such as tris (ethylenediamine) nickel (II) dichloride dihydrate and tris (ethylenediamine) nickel (II)

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dibromide dihydrate. FD and FAB spectra of the chloride measured for comparison are also described.

2. Experimental

The instrument used is the same as that reported previously,¹¹⁾ but some of experimental conditions are described briefly. A few μg of a sample (powder) is mixed

well with 1 μl of Nujol (liquid paraffin) on a glass plate until it becomes like a paste, and less than one tenths of the mixture is deposited on a needle tip (sample holder) heated at about 180°C by a heater surrounding the needle in the ion source. The needle is kept at about 1000 V as described in the previous paper.¹¹⁾

Shortly after introducing a sample (around 10 s), the sample ions are observed and recorded by a computer system (Shimadzu GCMS PAC 90) and/or a pen recorder. Usually lower resolution is used in order to record a mass spectrum up to high mass range with higher sensitivity. A part of mass spectrum was recorded repeatedly at a slow speed (30 s/scan) by a pen recorder with higher resolution (unit resolution) to measure isotope peak ratios. The samples (supplied from a laboratory of synthetic chemistry) were crystallized from an aqueous solution of nickel halide and ethylenediamine, containing two molecules of water of crystallization.

3. Results and Discussion

Mass spectra of $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{en})_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (en: ethylenediamine) are shown in Figs. 1 and 2, respectively. In both cases, the base peaks corresponding to protonated molecules, $(\text{Ni}(\text{en})_3 \text{X}_2) \text{H}^+$, are observed at m/z 309, 311, 313 and 315 for the chloride and at m/z

Fig. 1. Mass spectrum of tris (ethylenediamine) nickel (II) dichloride dihydrate
heater current; 1.45 A

Fig. 2. Mass spectrum of tris (ethylenediamine) nickel (II) dibromide dihydrate
heater current; 1.2 A

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397, 399, 401 and 403 for the bromide. Intense fragment ions at m/z 121 are a dimer of ethylenediamine, $(en)_2H^+$. During early period of heating, very weak peaks corresponding to the dihydrated molecular ions are observed as shown in Fig. 1, although their isotope ratios are slightly different from the natural abundances. No dihydrated molecular ions seems to be observed for the bromide (Fig. 2), because a group of ions at around m/z 440 did not always appear and their isotope ratios did not correspond to the natural abundances of the dihydrated ions of the bromide. The spectrum as shown in Fig. 1 is observed for 5–10 min at adequate heating, but if the temperature is either too high or too low, fragment ions such as $(en)_2H^+$ (m/z 121) and those at m/z 164 (probably $(en)_3H^+ - NH_3$) become dominant.

In the case of bromide, $(Ni(en)_2 Br)^+$ (m/z 257, 259,) and $(Ni(en)_2 Br_2)H^+$ (m/z 337, 339,) become more abundant at higher temperature. Small peaks observed at m/z 533, 535, and at m/z 593, 595, correspond to $(Ni_2(en)_3 Br_3)^+$ and $(Ni_2(en)_4 Br_3)^+$, respectively, which may be produced by the reactions between sample molecules and fragment ions at high temperature. Relative abundances of isotope peaks of the chloride at m/z 309, 311, 313, and 315 due to both nickel and chlorine isotopes reveal that these peaks correspond to $(Ni(en)_3 Cl_2)H^+$ ions but not to $(Ni(en)_3 Cl \cdot 2H_2O)^+$ ions. The observed values of isotope ratios are in good agreement with the values calculated from their natural abundances (Table I). This is consistent with the results for the bromide which did not show the peaks correspond-

Table I. Isotope Ratios of Protonated Molecular Peaks of Nickel Halide Complexes

	m/z	309	311	313	315
$(Ni(en)_3 Cl_2) \cdot H^+$	Calc.	100	104	42	9
	Obs.	100	102	40	10
$(Ni(en)_3 Cl \cdot 2H_2O)^+$	Calc.	100	72	19	4

	m/z	397	399	401	403
$(Ni(en)_3 Br_2)H^+$	Calc.	100	235	178	50
	Obs.	100	224	169	53

Fig. 3. Isotope peak patterns of $(Ni(en)_3 Br_2)H^+$

ing to $(Ni(en)_3 Br \cdot 2H_2O)^+$. The isotope peak pattern of the bromide shown in Fig. 3 and the observed isotope ratios are also in good agreement with the calculated values of $(Ni(en)_3 Br_2)H^+$ ions.

The chloride was measured by FD and FAB techniques, too. The protonated molecule $(Ni(en)_3 Cl_2)H^+$ was not observed in both spectra, while it is the base peak in the LI spectrum. Although the FD spectrum shows weak peaks in the area in which the dihydrated molecular ion peaks might appear, the isotope ratios of these peaks did not correspond to the expected values. Considering their isotope ratios and mass num-

bers, these are likely to be $(\text{Ni}_2(\text{en})_2\text{Cl}_3)^+$ (m/z 341,), but not the dihydrated molecular ions. Because the mass number of $(\text{Ni}_2(\text{en})_2\text{Cl}_3)^+$ corresponds to the sum of mass numbers of intense fragment ions, i.e., $(\text{Ni}(\text{en})\text{Cl}_2)^+$ (m/z 188), and $(\text{Ni}(\text{en})\text{Cl})^+$ (m/z 153), observed in the FD spectrum. Another abundant fragment ion was $(\text{en})\text{H}^+$.

In the case of FAB, a mass spectrum showing the structure of the chloride has not been obtained so far with glycerol as a matrix even by adjusting the pH, although there might be other better matrix.

4. Conclusions

The LI spectrum with a few μg of sample shows the molecular ions for 5 – 10 min that is enough to record isotope peaks by a pen recorder providing accurate measurement of isotope ratios. One of the advantages of this method is easy sample handling, e.g., fine powder mixed well with a matrix can be used. In general, however, a sample dissolved in a small amount of solvent prior to mixing with the matrix gives better results.

Several other types of metal complexes were also examined and their LI spectra showed molecular ions and a few fragment ions which provide information about the structure of the compound. The LI method seems to be useful for studies on metal complexes.

Acknowledgment

We wish to thank Prof. S. Yoshikawa for his kind gifts of nickel complexes and JEOL Co. for their help in measuring FD and FAB spectra.

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Keywords

Liquid ionization mass spectrometry
Nickel complex (ethylene diamine)
FD spectrum
Metal complex