CHEMISTRY LETTERS, pp. 1755-1758, 1985.

SECONDARY ION MASS SPECTROMETRY/METASTABLE ION SPECTRA OBTAINED BY LINKED SCAN TECHNIQUE AND FIELD DESORPTION MASS SPECTRA OF NONELECTROLYTE COMPLEXES, $[RuCl_2(bpy)_2]$ AND $[RuCl_2(phen)_2]^{1)}$

Mikio TANAKA* and Eiichi MIKI†
Laboratory of Chemistry, Nippon Medical School, Kosugi, Nakahara-ku,
Kawasaki 211
†Department of Chemistry, College of Science, Rikkyo University,
Nishi-Ikebukuro, Toshima-ku, Tokyo 171

The relative intensities of molecular ions and their isotopic peaks generated from the titled complexes were measured accurately by field desorption mass spectrometry. Secondary ion mass spectrometry/metastable ion spectra obtained by the linked scan technique gave useful information about the successive ligand-loss processes.

Field desorption (FD) mass spectrometry, fast atom bombardment (FAB) mass spectrometry, and secondary ion mass spectrometry (SIMS) are useful for characterizing low volatile organometallic complexes.[2,3] FD mass spectrometry is known to give data of molecular ion[4] and its isotopic peaks, but their relative intensities which reflect isotopic abundances of the elements in the complexes have not been measured accurately except in a few complexes.[2,5] FAB mass spectrometry and SIMS give data on the molecular ion and its fragmentation, but these data are complicated by contamination of the spectrum with matrix. On the other hand, MI (metastable ion) spectrum measured with the linked scan allows observation of only the fragment ions generated from the precursor ion. Hence, measurement of the MI spectrum gives clearer information on the molecular ion and its fragmentation data.

Ruthenium and chlorine atoms have seven and two stable isotopes, respectively. Therefore, the chemical composition of low volatile neutral compounds containing the two elements can be determined conveniently by comparison between the observed relative intensities of the molecular ion and its isotopic peaks, and the calculated ones. Hence, we have attempted to measure the accurate FD mass spectrum of $[\mathrm{RuCl_2L_2}]$ (L=bpy or phen) to identify the composition, and also to measure the SIMS/MI spectra by the linked scan technique to examine fragmentations characteristic of the ligands.

$[\mathrm{RuCl_2(bpy)_2}]\cdot 2\mathrm{H_2O}$ and $[\mathrm{RuCl_2(phen)_2}]$ were prepared by the methods reported by Tanaka et al.,6) and Bosnich and Dwyer,7) respectively. The FD mass spectra were measured by a combined FD unit on a Hitachi M-80 double-focusing mass spectrometer equipped with a Hitachi M-003 data processing system. The complexes were dissolved in dichloromethane and placed on a carbon emitter.8) The SIMS/MI spectra were measured by the mass spectrometer with a SIMS unit/ a linked scan unit. The complexes were placed on a silver plate probe tip as either a solution or suspension in glycerol. Xenon was used to produce the primary ion.9)

The FD mass spectrum of $[\mathrm{RuCl_2L_2}]$ showed only the molecular ion and its isotopic peaks. The observed relative intensities of the isotopic patterns agreed with the calculated ones to within 10%, as shown in Table 1. The calculated values were obtained from the isotopic abundances of ruthenium and chlorine atoms and then corrected with the contribution of isotopes of carbon, nitrogen, and hydrogen atoms. A similar result is also observed for the FD mass spectrum of $[\mathrm{RuCl(bpy)_2(CO)}]^+$.2) Analysis of the isotopic pattern was found to be one of the

Table 1. The observed and calculated relative intensities of the molecular ion and its isotopic peaks generated from $[\mathrm{RuCl_2L_2}]$ (L=bpy or phen) by FD mass spectrometry

$[\mathrm{RuCl_2(bpy)_2}]$

M/Z	478	479	480	481	482	483	484	485	486	487	488	489	490
Obsd a)	0.13	0.02	0.12	0.32	0.40	0.63	1.00	0.46	0.96	0.25	0.35	0.08	0.06
Calcd	0.12	0.03	0.12	0.30	0.38	0.64	1.00	0.51	0.99	0.28	0.41	0.10	0.07

$[\mathrm{RuCl_2(phen)_2}]$

M/Z	526	527	528	529	530	531	532	533	534	535	536	537	538
Obsd b)	0.10	0.01	0.08	0.30	0.38	0.58	1.00	0.49	0.94	0.25	0.38	0.06	0.02
Calcd	0.11	0.03	0.12	0.30	0.39	0.64	1.00	0.55	1.00	0.32	0.42	0.12	0.08

a) An average for 37 scans. b) An average for 79 scans.

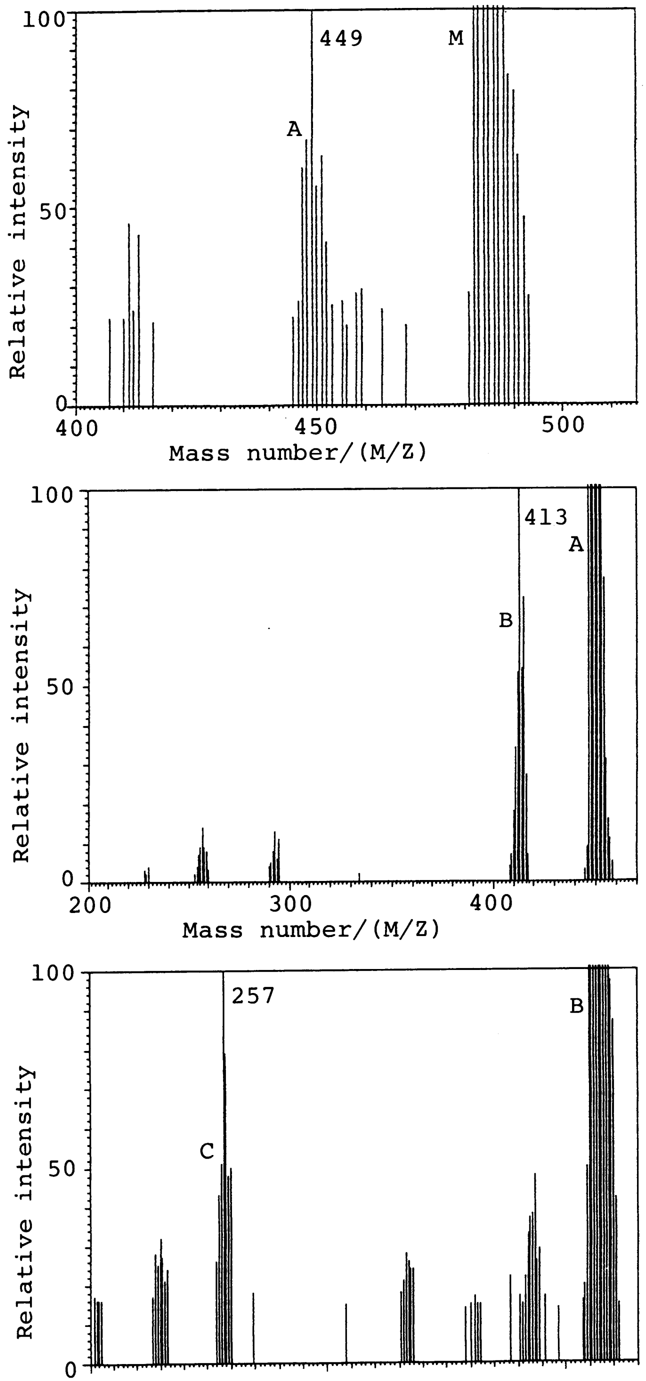

Fig. 1. The MI spectra of $[RuCl_2(bpy)_2]$ and its fragment ions by linked scan technique. M: The molecular ion (M/Z=484); M/Z=449: $(M-Cl)^+$; M/Z=413: $(M-2Cl-H)^+$; M/Z=257: $(M-2Cl-bpy-H)^+$.

most useful tools for measuring the molecular weight of low volatile neutral complex and determining its chemical composition.

The MI spectra obtained by the linked scan technique for $[RuCl_2(bpy)_2]$ are shown in Fig. 1. Isotopic peaks of the fragment ion (A) were found to be generated from the precursor ion (the molecular ion with M/Z=484) on the MI spectrum. When the fragment ion with M/Z=449 was used as a precursor ion, isotopic peaks of the fragment ion (B) were observed. Then, isotopic peaks of the fragment ion (C) generated from the precursor ion (the fragment ion with M/Z=413) were observed. The ions with the largest intensities in A, B, and C were M/Z=449, 413, and 257, respectively. These ions correspond to $(M-Cl)^+$, $(M-2Cl-H)^+$, and $(M-2Cl-bpy-H)^+$ as determined by the most abundant isotopes of ruthenium and chlorine, ^{102}Ru and ^{35}Cl. Consequently, the fragmentation patterns on the MI spectra can be interpreted by the following ligand-loss processes:

$$(M)^+ \xrightarrow{-Cl} (M-Cl)^+ \xrightarrow{-HCl} (M-2Cl-H)^+ \xrightarrow{-bpy} (M-2Cl-bpy-H)^+.$$

Similar ligand-loss processes were also observed for $[RuCl_2(phen)_2]$.

The SIMS spectrum of $[RuCl_2(bpy)_2]$ is shown in Fig. 2. Comparison of

Fig. 1 with Fig. 2 shows that the MI spectra measured by the linked scan technique make assignments of the fragment ions less ambiguous.

In conclusion, the above results confirmed the utility of the MI spectra obtained by the linked scan technique as a tool for rapid identification of nonelectrolyte complexes. This method is expected to be used more advantageously for the structural diagnosis of complicated coordination compounds.

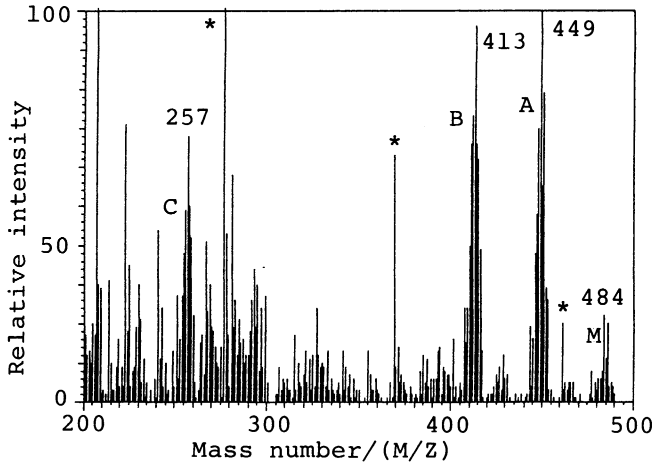

Fig. 2. The SIMS spectrum of $[RuCl_2(bpy)_2]$. M: The molecular ion (M/Z=484); M/Z=449: $(M-Cl)^+$; M/Z=413: $(M-2Cl-H)^+$; M/Z=257: $(M-2Cl-bpy-H)^+$. *derived from the matrix, glycerol.

References

1) Secondary ion mass spectrometry (SIMS) and field desorption (FD) mass spectrometry of metal complexes I.

2) R. L. Cerny, B. P. Sullivan, M. M. Bursey, and T. J. Meyer, Inorg. Chem., 24, 397 (1985).

3) J. Pierce, K. L. Busch, R. A. Walton, and R. G. Cooks, J. Am. Chem. Soc., 103, 2583 (1981).

4) Molecular ion is defined as the ion with the largest intensity.

5) D. E. Games, J. L. Gower, M. Gower, and L. A. P. Kane-Maguire, J. Organomet. Chem., 193, 229 (1980).

6) M. Tanaka, T. Nagai, E. Miki, K. Mizumachi, and T. Ishimori, Nippon Kagaku Kaishi, 1979, 1112.

7) B. Bosnich and F. P. Dwyer, Aust. J. Chem., 19, 2229 (1966).

8) The emitter currents: 15-25 mA; the emitter potential: 3 kV; the cathode potential: -4 kV; the ion accelerating potential: 3 kV.

9) The ionization method: electron impact; the primary ion accelerating potential: 8-10 kV.

(Received August 28, 1985)