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Studies on Mass Spectrometry of Metal Chelates. II.[1] Mass Spectrometric Investigation of Thiooxine Metal Chelates

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In every mass spectrum of the metal thiooxinates, the peak being attributable to the molecular ion was observed, and the mass units correspond to a 2: 1 molar ratio chelate (ligand: metal). The loss of 160 mass units from the molecular ion was observed. This indicates that a cleavage of one molecule of the coordinated thiooxine from the molecular ions affords the fragment ion of a 1: 1 ratio chelate. In the following fragmentation process, the group of Mn, Co, Ni, Cu, and Pd chelates and the group of Zn, Cd, Hg, and Pb chelates showed different pathway. In order to examine the stabilities of these metal thiooxinates under electron impact, the intensity ratio of a fragment ion peak of a 1: 1 molar ratio chelate to a molecular ion peak was calculated and the following decreasing stability order in the central metal atom was observed; Cd>Zn>Ni>Pd∼Co>Mn>Cu>Hg>Pb. This order is found to be quite similar to that of metal oxinates, reported in a previous paper. A definite correlation between these intensity ratios and the charge-radius ratio, *e/r*, and the ionization potential of the central metal atoms was shown.

With an aim to apply mass spectrometry to the investigation of metal chelates, 8-quinolinol (oxine) chelates with the divalent metals, Mn, Co, Ni, Cu, Zn, Pd, and Pb, were previously studied.[1] The stabilities of oxine metal chelates under electron impact were observed to be the following order of the central metals; Zn>Ni>Co∼Pd>Mn>Cu>Pb. It was also found that the peak intensities of the molecular ions have a close relation with the charge-radius ratio, *e/r*, of the metal atom of the chelates. This paper is chiefly concerned with the mass spectrometric studies of 8-quinolinethiol (thiooxine) chelates with the divalent metals, Mn, Co, Ni, Cu, Zn, Pd, Cd, Hg, and Pb, and to a comparison with those of oxine metal chelates.

Results and Discussion

1. Fragmentation of Thiooxine

The mass spectrum of thiooxine is shown in Table I. Main peaks in the mass spectrum of thiooxine were observed at *m/e* 161, 117, and 90. The peak at *m/e* 117 is ascribable to the fragment ion produced by the loss of 44 mass units, corresponding to CS, from the molecular ion at *m/e* 161. Then a fragment ion peak due to the loss of 27 mass units, which corresponds to HCN, was observed at *m/e* 90. The main fragmentation process of thiooxine is shown in Chart 1. This process is quite similar to that of oxine, reported by Clugston and MacLean.[3] The peak at *m/e* 128 may be produced by the removal of the SH group from the molecular ion. In the case of oxine, no cleavage of the OH group was observed. Peak at *m/e* 160 is due to the loss of H· from the molecular ion, although this pathway was not observed for oxine. These appear to be the main difference between the two ligands.

2. Fragmentation of Metal Thiooxinates

The mass spectra of metal thiooxinates are shown in Table II. Every spectrum shows a peak of the molecular ion (I) as a 2: 1 ratio chelate in a higher mass region. The loss of 160

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[1] Part I: Y. Kidani, S. Naga, and H. Koike, *Bull. Chem. Soc. Japan*, 46, 2105 (1973).

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[3] D.M. Clugston and D.B. MacLean, *Can. J. Chem.*, 44, 781 (1966).

mass units from I occurred in every chelate, indicating to yield the fragment ion (II) of a 1: 1 chelate with the cleavage of one molecule of coordinated thiooxine from I. These fragmentation processes of metal thiooxinates are quite similar to those of metal oxinates. In the case of Mn, Co, Ni, Cu, and Pd chelates, the loss of 44 mass units from the ion (II) was observed. From the fragmentation pathway of the ligand, this may be attributable to the loss of CS. This interpretation is supported by the presence of a metastable ion peak; for example, Ni-(thiooxine)$_2$ showed the metastable ion peak at 140 (Calcd. 139.8), supporting the fragmentation path from *m/e* 218 to *m/e* 174. For metal oxinates of Mn, Co, Ni, Cu, and Pd, the loss of CO was also observed. The fragmentation pathway from the ion (II) to (IV) was recognized by the presence of metastable ion peak, Zn(thiooxine)$_2$; *m/e* 224—*m/e* 160, Calcd. 114.3, Found 114.0, although the fragment ion (*m/e* 144) corresponding to the loss of metal from a 1: 1 chelate ion was not observed for metal oxinates. The fragmentation pathways of metal thiooxinates are shown in Chart 2. There are two pathways for the fragmentation of II; the one gives the ion (III) by the loss of CS, and the other yields the ion (IV) by the loss of metal. The ions of Mn, Co, Ni, Cu, and Pd chelates gave both of fragment ions (III) and (IV),

TABLE I. Mass Spectrum of Thiooxine

m/e	Rel. Int.	Ion
161	100	M$^+$
160	25	M$^+$–H
128	26	M$^+$–SH
117	96	M$^+$–CS
101	15	(M$^+$–SH)–HCN
90	26	(M$^+$–CS)–HCN

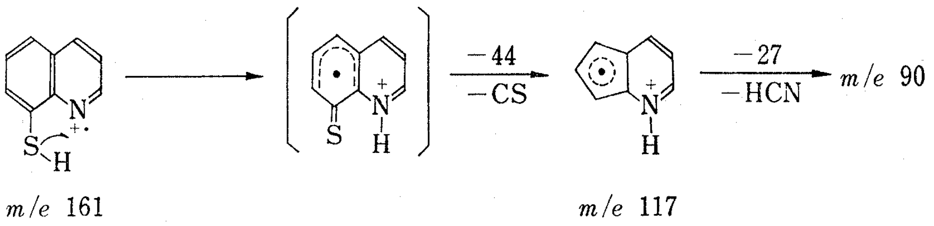

Chart 1. Fragmentation of 8-Quinolinethiol

TABLE II. Mass Spectra of Thiooxine Metal Chelates

Metal	Ion				
	M$^+$ *m/e*[d] (%)[e]	M$^+$–L[a] *m/e* (%)	(M$^+$–L)–CS *m/e* (%)	*m/e* 161[b] (%)	*m/e* 160[c] (%)
Mn	375(22)	215 (33)	171(10)	(100)	(40)
Co	379(48)	219 (59)	175(21)	(66)	(36)
Ni	378(96)	218(100)	174(53)	(38)	(38)
Cu	383(35)	223 (78)	179(12)	(100)	(49)
Zn	384(35)	224 (32)	—	(60)	(100)
Pd	426(22)	266 (28)	222(14)	(34)	(49)
Cd	434(20)	274 (11)	—	(32)	(100)
Hg	522(14)	362 (43)	—	(26)	(100)
Pb	528(12)	368(100)	—	(10)	(30)

[a] coordinated thiooxine (160 mass units)
[b] the molecular ion of the thiooxine (C_9H_7NS)
[c] the thiooxinate ion(C_9H_6NS)
[d] *m/e* values are given for the ions containing ^{58}Ni, ^{63}Cu, ^{64}Zn, ^{106}Pd, ^{114}Cd, ^{202}Hg, and ^{208}Pb
[e] relative intensity

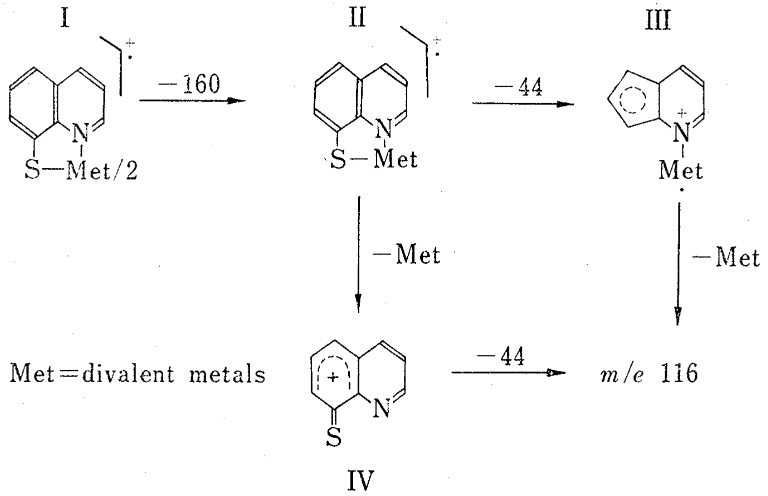

Chart 2. Fragmentation of Divalent Metal Thiooxinates

while those of Cd, Zn, Hg, and Pb chelates take only one fragmentation pathway from the ion (II) to (IV). The peak at m/e 161 may be caused by the thiooxine molecule which is produced by the thermal decomposition, prior to the vaporization of the metal thiooxinates, in a similar manner to that of the metal oxinates.[1]

3. Stability under Electron Impact

In order to examine the stabilities of metal thiooxinates under electron impact, the peak intensities of the molecular ion (I) and the fragment ion (II) were compared, because the ions (I) and (II) may be strongly influenced by the electronic configuration of their central metal atoms. To compare the stability of I for these metal thiooxinates in the fragmentation process from I to II, the peak intensity of the molecular ion was calculated by I/(I+II), as shown in Table III. The magnitudes of the peak intensity of I decrease in the following order of the central metal atoms, $\mathrm{Cd}>\mathrm{Zn}>\mathrm{Ni}>\mathrm{Pd}\sim\mathrm{Co}>\mathrm{Mn}>\mathrm{Cu}>\mathrm{Hg}>\mathrm{Pb}$. The stabilities of metal thiooxinates under electron impact have a similar tendency to those of metal oxinates.[1] The values of the intensity ratio of I to I+II for metal thiooxinates are generally found to be smaller than those for oxinates. This may be partly caused by the difference in the atoms, oxygen and sulfur, coordinating with the central metal atoms.

Table III. Peak Intensity of the Molecular Ion

		Cd	Zn	Ni	Co	Pd	Mn	Cu	Hg	Pb
I/(I+II)%	oxine	—	67	63	61	61	55	48	—	22
	thiooxine	66	52	48	45	45	39	30	25	12

Thus, Fig. 1 shows the correlation between the charge-radius ratio (e/r) of the central metal atoms[4] and the intensity ratios, which are tabulated in Table III. This indicates that the peak intensity ratios increase proportionally with the values of e/r of the central metal atoms. It is considered that in metal chelates the stability of the molecular ion under electron impact is strongly affected by the value of e/r of the central metal atoms. In Fig. 1, Cd-thiooxinate deviates considerably away from this line. A similar phenomenon was observed in the case of Cd-oxinate.[5] This may be caused by the characteristics of the Cd atom. For Cd chelate, it is necessary to take another factor rather than e/r and a detailed investigation is attempted.

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[4] Pauling's value was taken for ionic radii.

[5] Unpublished data.

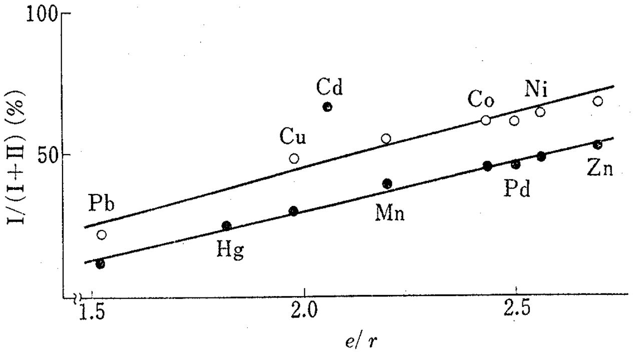

Fig. 1. Correlation between the Charge-radius Ratio and the Intensity Ratio

—○—: oxine metal chelate
—●—: thiooxine metal chelate

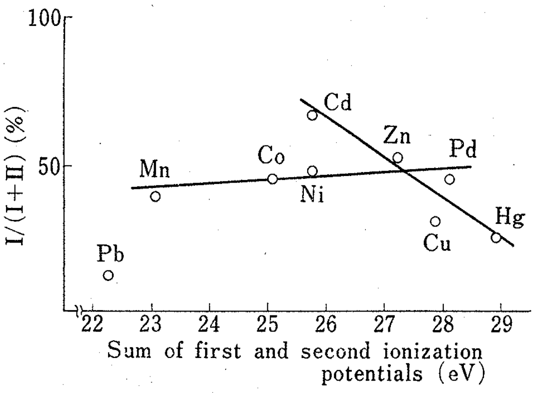

Fig. 2. Correlation between the Ionization Potential and the Intensity Ratio

On the other hand, Martell, *et al.*,[6] reported that the sum of the first and second ionization potentials of the central metal atoms had a linear relationship to the stability constants in solution. It may be inferred that the stabilities of the metal tiooxinates under electron impact have a correlation with the ionization potentials of their metal atoms. Therefore, the peak intensity ratios of I to I+II were plotted against the sum of the first and second ionization potential values (Fig. 2).[7] As shown in Scheme II, the group of Mn, Co, Ni, Cu, and Pd thiooxinates and the group of Cd, Zn, and Hg thiooxinates had a different fragmentation process. In these two groups, it is considered that the relationships between the ionization potential and the peak ratio show also some different tendencies. It is shown that two groups have a linear relation, respectively. The difference in the behaviors of these two groups had been found in IR spectra of the metal chelates. According to the IR studies of metal oxinates by Charles, *et al.*,[8] and metal thiooxinates by Mido, *et al.*,[9] the frequency of the metal-sensitive band of the ligand in the IR spectra was plotted against the atomic weight of central metal atoms. These frequencies of the transition metal chelates with thiooxine and oxine shift remarkably as the atomic weight of the metal increases, while the frequencies of another group of Zn, Cd, and Hg chelates shift slightly. This indicates the involvement of 3*d*-orbitals in the metal-ligand bonding for the transition metal chelates. In the fragmentation the fact mentioned above may suggest a difference between the electronic configurations of the two groups.

In conclusion, it has been noticed that both divalent metal oxinates and thiooxinates show similar trends to the stability under electron impact in the following decreasing order of the central metal atom, Zn>Ni>Pd∼Co>Mn>Cu>Pd. The molecular ion of each metal oxinate is considered to be generally more stable than that of each corresponding metal thiooxinate under similar experimental conditions. This may be caused by the difference of the atoms coordinating to the central metal atoms, especially the difference between oxygen and sulfur in electronegativity. In the case of thiooxine metal chelates, a close correlation between the stability under electron impact and charge-radius ratio of the central metal atoms has been found. It is considered that in mass spectra of metal chelates the stability of the molecular ion is strongly affected by the charge-radius ratio of central metal atoms. A plot of the stability under electron impact against the ionization potential of the central metal

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[6] A.E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1952, p. 188.

[7] Ionization potentials were taken from: "Iwanami Rikagaku Jiten," 3rd ed., Iwanami-shoten, Tokyo, 1971, p. 1508.

[8] R. G. Charles, H. Freiser, R. Friedel, L.E. Hilliard, and W.D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

[9] Y. Mido and E. Sekido, *Bull. Chem. Soc. Japan*, **44**, 2130 (1971).

atoms suggests that there would be a difference between the group of Mn, Co, Ni, Cu, and Pd chelates and the group of Cd, Zn, and Hg chelates in the electronic configuration of II.

Experimental

Materials——Divalent metal thiooxinates were prepared according to the method by Dalziel, *et al.*,[10] and the composition of each metal chelate was confirmed by elementary analysis. Their infrared spectra were in accordance with the data reported by Mido, *et al.*[9]

Apparatus and Conditions——Measurements were made with a Hitachi RMU-7 double focusing mass spectrometer. The conditions are: sample introduction is by means of the direct inlet system; ionizing voltage is 70 eV; ion accelerating voltage is 1800 V; total emission current is 80 μA, and ion source temperature is 250°.

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[10] J.A.W. Dalziel and D. Kealey, *Analyst*, **89**, 411 (1964).