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Studies on Mass Spectrometry of Metal Chelates. III. Mass Spectrometry of 2-, 4-, 5-, 7-Methyl-, and 5-Chloro-oxine Metal Chelates

Shinobu Naga, Yoshinori Kidani, and Hisashi Koike*

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467

**School of Medical Technology and Nursing, Fujita Gakuen University, Toyoake, Aichi 470-11*

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For application of mass spectrometry to metal chelate chemistry, a group of divalent metal chelates (Co, Ni, Cu, Zn, and Pd) of 2-Me-oxine, 4-Me-oxine, 5-Me-oxine, 7-Me-oxine, and 5-Cl-oxine has been investigated. 2-Methyloxine and 4-Me-oxine of these ligands give similar spectra and are considered to have similar fragmentation patterns. The same was found for 5-Me-oxine and 7-Me-oxine. However, the spectra of 2-Me-oxine and 4-Me-oxine metal chelates differ from each other, as do also the spectra of 5-Me-oxine and 7-Me-oxine. Thus fragmentation patterns may vary with the metal chelate formation of the ligands even when they have the same fragmentation patterns. Each metal chelate gave two peaks corresponding to metal-containing ions, a molecular ion (I) of a 2:1 (ligand: metal) chelate, and a fragment ion (II) of a 1:1 chelate due to the loss of a ligand radical from ion I. In the case of Co, Ni, Zn, and Pd chelates of 2-Me-oxine, a peak corresponding to the loss of a methyl radical from I was observed, apparently caused by steric effect. In the metal chelates of 5-Me-oxine, a peak corresponding to the loss of a hydrogen radical from I was also observed. However, the fragmentation pathway of formation of II from I is commonly observed in all metal chelates. Since this pathway is comparable with the second successive formation reaction (k_2) in solution, the peak intensity ratio of the ion of I to that of II was calculated. From the results it was found that the stability of the chelates decreases in the order Zn>Ni>Pd∼Co>Cu and that it depends on the charge-radius ratio (e/r) of the central metal ion, or the stability constant ($\log k_2$) observed in solution.

We have studied the divalent metal chelates of 8-quinolinol (oxine)[1] and 8-quinolinethiol (thiooxine)[2] and estimated the stability of these metal chelates under electron impact from the intensity ratio of the peaks. It was found that the stability of these oxine and thiooxine metal chelates is in the order Zn>Ni>Pd∼Co>Mn>Cu>Pb and that it depends on the charge-radius ratio (e/r) of the central metal ion.

The results of mass spectral analysis of divalent metal chelates of 2-methyl-8-quinolinol (2-Me-oxine), 4-methyl-8-quinolinol (4-Me-oxine), 5-methyl-8-quinolinol (5-Me-oxine), 7-methyl-8-quinolinol (7-Me-oxine), and 5-chloro-8-quinolinol (5-Cl-oxine) are reported.

Results and Discussion

Mass Spectra of Ligands and Their Fragmentation Patterns. The mass spectra of 2-Me-oxine, 4-Me-oxine, 5-Me-oxine, 7-Me-oxine, and 5-Cl-oxine are shown in Fig. 1.

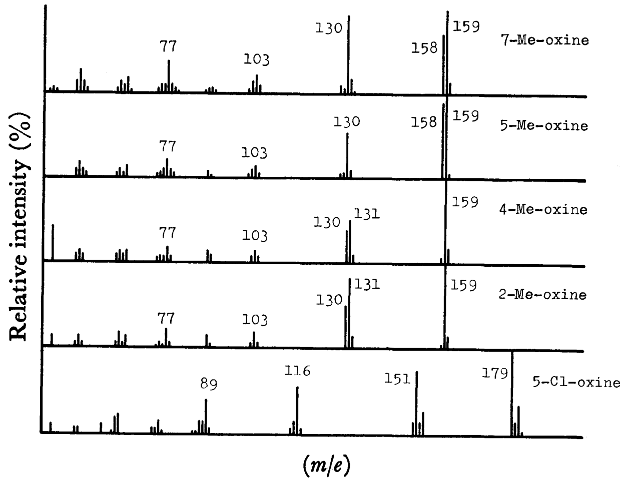


Fig. 1. Mass spectra of oxine derivatives.

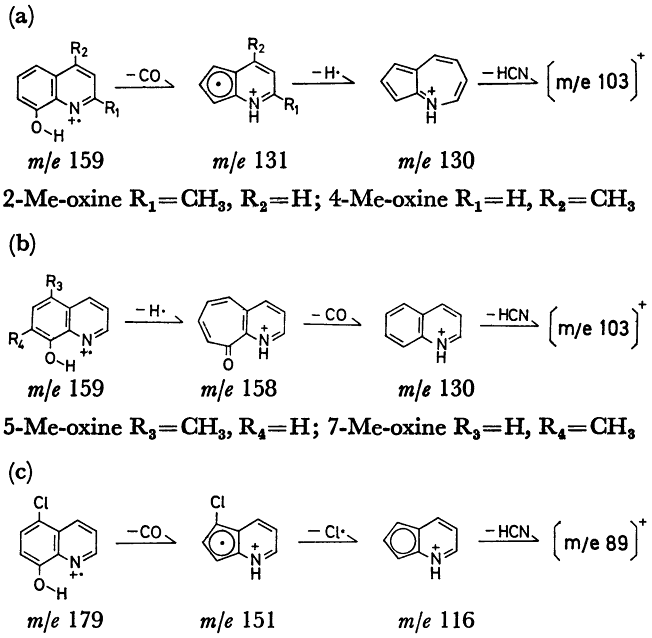
Each spectrum gives a strong molecular ion peak (2-, 4-, 5-, and 7-Me-oxine: m/e 159; 5-Cl-oxine: m/e 179).

The spectrum of 2-Me-oxine is similar to that of 4-Me-oxine, both ligands having fragment ion peaks at m/e 131, 130, and 103. The fragmentation patterns of 2-Me-oxine and 4-Me-oxine were reported by Stevenson *et al.*[3] (Scheme 1-a). The molecular ion loses CO to give an ion of m/e 131, and then this ion loses H· to produce an azatropylium type ion of m/e 130, which in turn loses HCN to produce an ion of m/e 103.

Similar spectra are also observed for 5-Me-oxine and 7-Me-oxine, both having the strongest peak, except the molecular ion peak, at m/e 158 (M^{+}-1); main fragment ion peaks can be observed at m/e 130 and 103. The peak at m/e 158 is the one corresponding to the loss of H· from the molecular ion, and is due to a tropylium type ion (Scheme 1-b). The peak at m/e 130 is due to the ion produced by the loss of CO from the ion of m/e 158. The ion of m/e 130 might lose HCN to produce an ion of m/e 103.

5-Chlorooxine shows main fragment ion peaks at m/e 151, 116, and 89. The difference between the molecular ion peak and the peak at m/e 151 is 28, corresponding to the loss of CO from the molecular ion. It appears that the peak at m/e 116 is due to the ion produced by the loss of Cl· from the ion of m/e 151. The peak at m/e 89 seems to be due to the ion produced by the loss of HCN from the ion at m/e 116. The fragmentation patterns of these oxine derivatives are summarized in Scheme 1-a, b, and c.

In the case of oxine derivatives with a methyl group on its pyridine ring, the molecular ion initially loses CO and then H· to produce an azatropylium type ion. On the other hand, in the case of oxine derivatives with a methyl group on its benzene ring, the molecular ion initially loses H· to produce a tropylium type ion, which then loses CO in succession. A distinct dif-



Scheme 1. Fragmentation of oxine derivatives.

ference in fragmentation patterns was found between the two cases. However, it was difficult to find a difference between 2-Me-oxine and 4-Me-oxine and between 5-Me-oxine and 7-Me-oxine from their mass spectra.

The values calculated and found for the metastable ion peaks observed in each fragmentation pathway (Scheme 1) are summarized in Table 1.

TABLE 1. METASTABLE ION PEAKS IN THE MASS SPECTRA OF OXINE DERIVATIVES

Compound	Transition	m* Calcd.	m* Found	Expelled fragment
5-Cl-oxine	179→151+28	127.38	127.1	CO
	151→116+35	89.11	—	Cl·
	116→ 89+27	68.28	68.3	HCN
2-Me-oxine	159→131+28	107.93	108.0	CO
	131→130+ 1	129.01	129.0	H·
	130→103+27	81.61	81.5	HCN
4-Me-oxine	159→131+28	107.93	108.0	CO
	131→130+ 1	129.01	129.0	H·
	130→103+27	81.61	81.5	HCN
5-Me-oxine	159→158+ 1	157.01	157.0	H·
	158→130+28	106.96	107.0	CO
	130→103+27	81.61	81.5	HCN
7-Me-oxine	159→158+ 1	157.01	157.0	H·
	158→130+28	106.96	107.0	CO
	130→103+27	81.61	81.5	HCN

Mass Spectra of Divalent Metal Chelates and Their Fragmentation Patterns. *2-Me-oxine Metal Chelates*: Figure 2 shows the spestra of Ni, Co, Cu, Zn, and Pd chelates with 2-Me-oxine. Molecular ion peaks of chelates were observed in the highest mass region of all the spectra, showing that the ligand and metal are combined in a 2: 1 molar ratio. Except for Cu chelate, a fragment ion peak due to the loss of CH_3· from the molecular ion is observed. On the other hand, all spectra have a peak corresponding to the loss of 158 amu (one molecule of 2-Me-oxine) from the molecular ion, the peak due to the ion having a 1: 1 ligand to metal ratio. Another peak due to the loss of H· from this ion, which appears to be azatropylium type ion, is observed. The loss of CO from this ion takes place except for Zn chelate. The fragmentation pattern of 2-Me-oxine metal chelates is shown in Scheme 2.

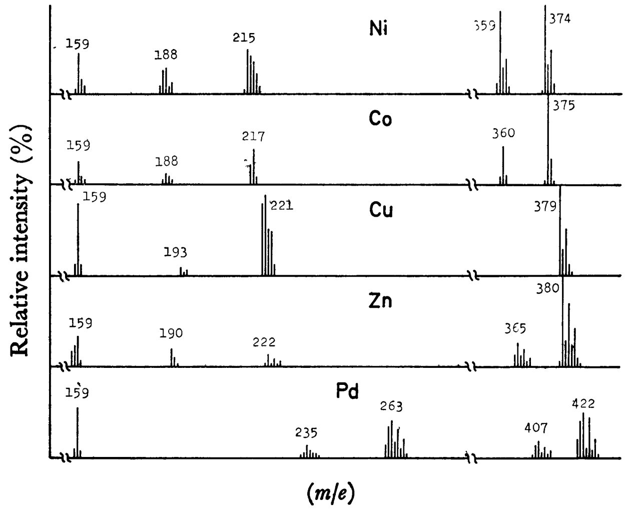
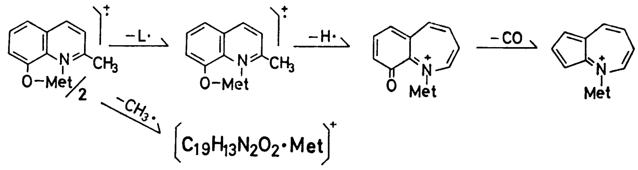


Fig. 2. Mass spectra of 2-Me-oxine metal chelates.



Met=divalent metals

Scheme 2. Fragmentation of 2-Me-oxine metal chelates.

4-Me-oxine Metal Chelates: Figure 3 and Scheme 3 show the spectra of Ni, Co, Cu, Zn, and Pd chelates with 4-Me-oxine and their fragmentation patterns. The molecular ion peak of each chelate corresponding to a 2: 1 ligand to metal ratio was observed in the highest mass region of all the spectra, followed by a fragment ion peak due to the loss of one molecule of 4-Me-oxine

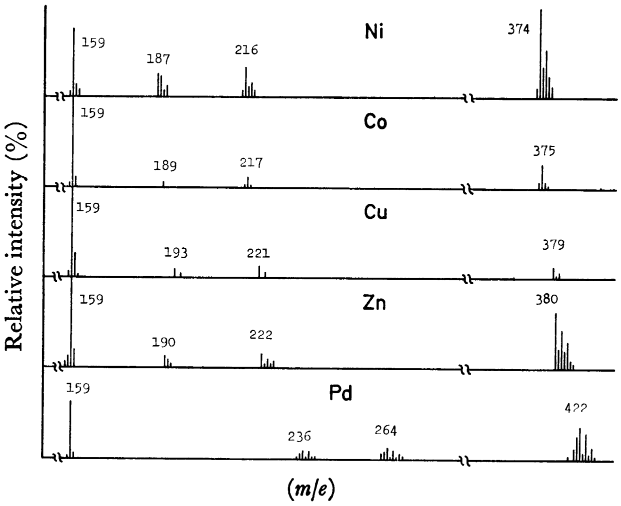
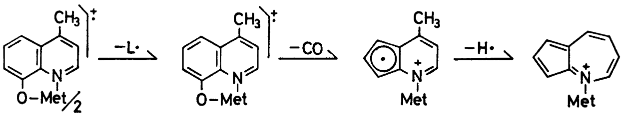


Fig. 3. Mass spectra of 4-Me-oxine metal chelates.



Met=divalent metals

Scheme 3. Fragmentation of 4-Me-oxine metal chelates.

(158 amu), and with a 1: 1 ligand to metal ratio. Except for the Zn chelate the peak was followed by another peak corresponding to the loss of CO from the 1: 1 chelate ion.

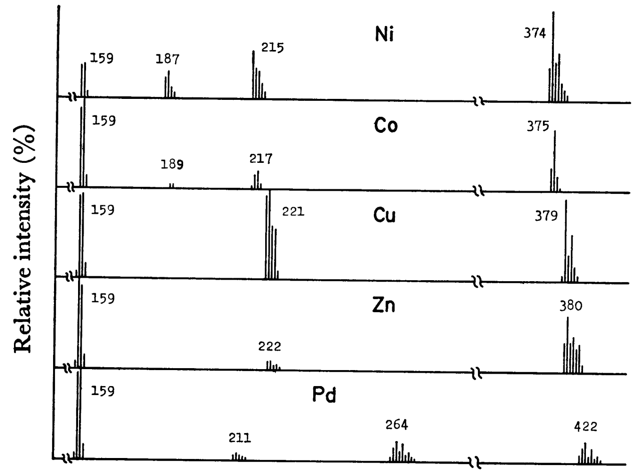
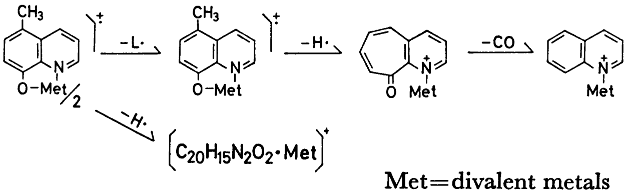


Fig. 4. Mass spectra of 5-Me-oxine metal chelates.

5-Me-oxine Metal Chelates: Figure 4 shows the spectra of Ni, Co, Cu, Zn, and Pd chelates with 5-Me-oxine. The molecular ion peak of each chelate corresponding to a 2: 1 ligand to metal ratio was observed in the highest mass region of all the spectra, followed by a peak corresponding to the loss of one amu (corresponding to $H^{\dagger}$). The ion $M^{\dagger}-1$ would have a mixed ligand complex structure since either of the two ligands can lose a hydrogen to form tropylium type structure. On the other hand, a fragment ion peak corresponding to the loss of 158 amu from the molecular ion also appears with a 1: 1 ligand to metal ratio. The peak is followed by another peak, which seems to be a tropylium type ion by the loss of H· from that ion. This is followed by a fragment ion peak corresponding to the loss of CO from tropylium type ion except for Zn chelate, the fragment ion peak being weak (Scheme 4).



Met=divalent metals

Scheme 4. Fragmentation of 5-Me-oxine metal chelates.

7-Me-oxine Metal Chelates: Figure 5 shows the spectra of Ni, Co, Cu, Zn, and Pd chelates with 7-Me-oxine. The loss of 158 amu, one molecule of 7-Me-oxine, from the molecular 2: 1 chelate ion appears to give a fragment ion peak corresponding to a 1: 1 lignad to metal ratio. This is followed by a peak with high intensity, corresponding to the loss of H· from the 1: 1 chelate ion. The peak with low intensity resulting from the loss of 28 amu corresponding to CO is observed in the spectra except for Zn chelate (Scheme 5).

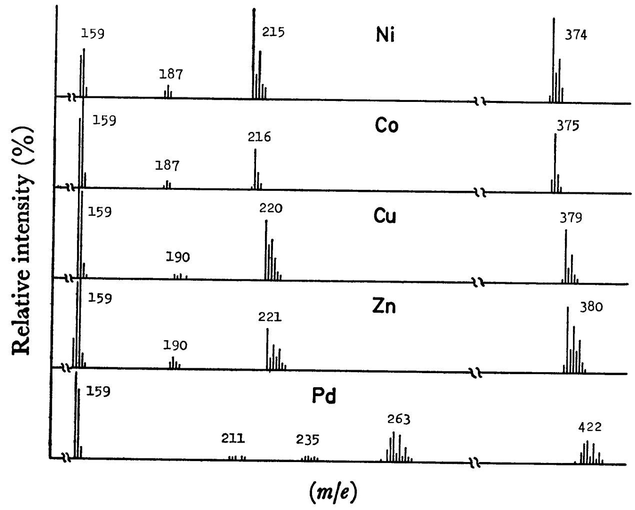
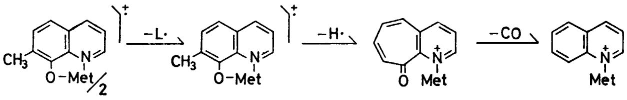


Fig. 5. Mass spectra of 7-Me-oxine metal chelates.



Met=divalent metals

Scheme 5. Fragmentation of 7-Me-oxine metal chelates.

5-Cl-oxine Metal Chelates: Figure 6 shows the spectra of Ni, Co, Cu, Zn, and Pd chelates with 5-Cl-oxine. The molecular ion peak of each chelate was observed in the highest mass region of all spectra corresponding to a 2: 1 ligand to metal ratio. A fragment ion peak due to the ion produced by the loss of 178 amu from the molecular ion was also observed. Since 178 amu corresponds to one molecule of 5-Cl-oxine, the ion produced has a 1: 1 ligand to metal molar ratio. Except

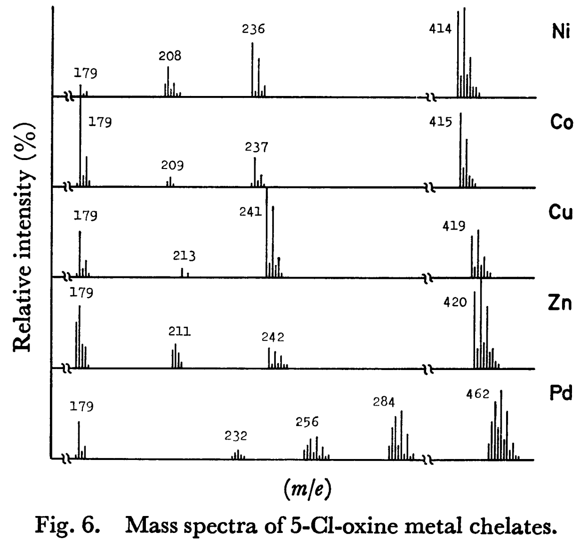
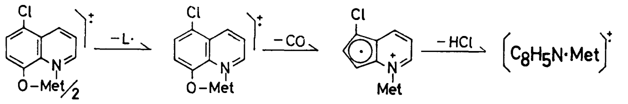


Fig. 6. Mass spectra of 5-Cl-oxine metal chelates.



Met=divalent metals

Scheme 6. Fragmentation of 5-Cl-oxine metal chelates.

for Zn chelate, the loss of 28 amu corresponding to CO from the 1:1 chelate ion is observed. The peak is followed by a fragment ion peak which lost HCl. The fragmentation pattern is shown in Scheme 6.

The fragmentation patterns of 2-Me-oxine and 4-Me-oxine and those of 5-Me-oxine and 7-Me-oxine are similar to each other, but the metal chelates of these methyloxine derivatives show fairly different fragmentation patterns. In the case of 2-Me-oxine, a fragment ion peak due to the loss of $CH_3\cdot$ from the molecular ion can be observed, but in that of 4-Me-oxine metal chelates no corresponding fragmentation occurred. A peak corresponding to the loss of H· from the molecular ion was observed in the case of 5-Me-oxine, but not in that of 7-Me-oxine.

In each spectrum the loss of either H· or CO from the 1:1 fragment ion was observed. The fragment ions produced are expected to contain a metal atom combined with the nitrogen atom. Thus, in the 1:1 fragment ion, the metal atom seems to be bound more strongly with the nitrogen atom than with the oxygen atom. However, each Zn chelate shows no loss of CO from the 1:1 fragment ion or from the fragment ion produced by the loss of H· from the 1:1 ion. This may be related to the valence change of the metal in the fragmentation process for acetylacetone metal chelates.[4] According to the classification of metals by Budzikiewicz *et al.*,[5] the valence change in Zn seems to be difficult, and the oxygen-zinc bond might be stronger than the other oxygen-metal bond, resulting in the difficult loss of CO.

The loss of $CH_3\cdot$ from the molecular ion occurs in Co, Ni, Zn, and Pd chelates of 2-Me-oxine only. The fragmentation pathway is not observed for the other methyloxine metal chelates. This may be partly caused by a steric influence of the methyl group at 2-position on the quinoline ring. Thus, in gaseous state the molecular ions of Co, Ni, Zn, and Pd chelates with 2-Me-oxine might take such a sterically hindered structure, which favors the loss of the methyl group.

Each spectrum of the metal chelates includes the peaks due to the ligand itself. It seems that prior to vaporization the chelate is thermally decomposed and the peak due to the ligand itself may be observed together.[1]

Stability under Electron Impact. Various metal chelates of mono-methyl-oxine derivatives show different fragmentation patterns depending on the position of the methyl group. However, a fragmentation pathway common to all the metal chelates can be observed, *i.e.*, the pathway in which a ligand radical is lost initially from a 2:1 molecular ion (I) to transform into a 1:1 fragment ion (II). This fragmentation pathway can be compared with the second successive formation reaction of metal chelates in solution. Thus, in order to examine the stability of ion I under electron impact, the peak intensity of I was calculated as the intensity ratio of I to the sum of I and II (Table 2). The peak intensity of I for each ligand is in the order: Zn>Ni>Pd~Co>Cu. This suggests that the peak intensity is related to the characteristics of the central metal ions and not to those of the ligands in the chelates. The values in Table 2 are plotted against the charge-radius ratio (e/r) of the central metal ions,[6] *viz.*, charge density, which is known to affect the stability of metal chelate in solution (Fig. 7).[7] We see that the peak intensity of I is proportional to the charge density; even under electron impact the molecular ion of a metal chelate having a central metal ion of high charge density is more stable than that of another chelate having a metal ion of low charge density.

TABLE 2. INTENSITY RATIOS OF THE MOLECIULAR ION, I, TO THE FRAGMENT ION, II.

Ligand	Metal				
	Zn	Ni	Pd	Co	Cu
oxine[1]	67	63	61	61	48
thiooxine[2]	52	48	45	45	30
2-Me-oxine	87	77	75	74	55
4-Me-oxine	86	75	75	74	56
5-Me-oxine	75	69	67	65	50
7-Me-oxine	85	77	74	75	57
5-Cl-oxine	65	62	58	57	43

Based on the assumption that the fragmentation pathway from I to II is correlated to the formation process of a 1:1 chelate from a 2:1 chelate in solution, which is expressed in terms of the stability constant,

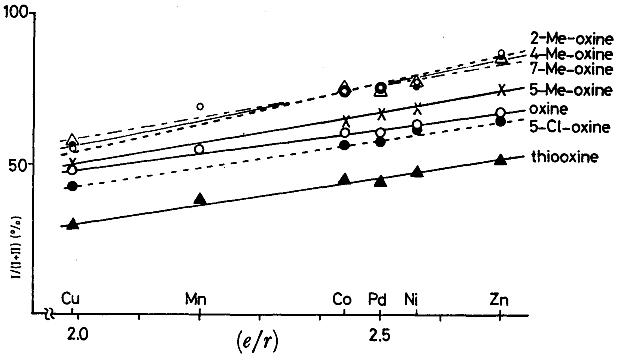


Fig. 7. Correlation between the intensity ratios and the charge-radius ratios of metals.

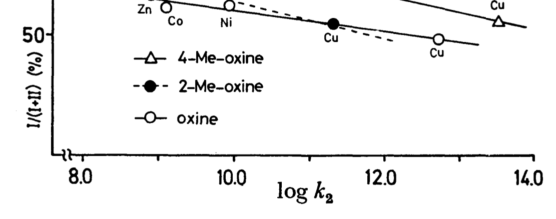


Fig. 8. Correlation between the intensity ratios and stability constants, log k_2.

$\log k_2$, a close relation between the stability of I under electron impact and $\log k_2$, is expected. The values in Table 2 are plotted against $\log k_2$ (Fig. 8).[8] A linear relation holds between the stability of I under electron impact and $\log k_2$ in the metal chelates of 4-Me-oxine, 2-Me-oxine, and oxine. 5-Methyloxine, 7-Me-oxine, and 5-Cl-oxine are not included, since the values of $\log k_2$ are not known.

We can thus distinguish the metal chelates of similar methyl-oxine derivatives, and the molar ratio of ligand to metal in a chelate can be simply determined with a minute quantity of sample. It is possible to identify the metal contained from the isotope ratio in the molecular ion peak. By further detailed examinations of the spectra, the stability of the metal chelates under electron impact can also be studied. All these results indicate that mass spectrometry can be applied effectively to investigations of the metal chelates with methyl-oxine derivatives.

Experimental

Apparatus: Mass spectra were measured with a Hitachi RMU-7 mass spectrometer by means of a direct inlet system, at 70 eV ionization voltage.

Reagents: 2-Methyl-oxine and 5-Cl-oxine (reagent grade, Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. 4-Methyl-oxine,[9] 5-Me-oxine,[10] and 7-Me-oxine[10] were synthesized according to the reported methods.

Syntheses of Metal Chelates: Alcohol solutions of metal chlorides were added to alcohol solutions of the ligands. The mixtures were warmed on a water bath and the resulting precipitates were separated by filtration. After washing with hot alcohol and water several times, the precipitates were dried at *ca.* 110 °C under reduced pressure. The composition of each metal chelate was confirmed by elemental analysis.

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