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Studies on Mass Spectrometry of Metal Chelates. I. Mass Spectrometry of Oxine Metal Chelates[1]

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With a view to applying mass spectrometry to the studies of metal chelates, we investigated the mass spectrometry of divalent metal oxinates (Mn, Co, Ni, Cu, Zn, Pb, and Pd). The molecular ion I, whose peaks correspond to the metal chelates in a 2: 1 ratio, were observed in every spectrum. A loss of 144 mass units from I, corresponding to one molecule of coordinated oxine, occurred to afford the fragment ions II of metal chelates in a 1: 1 ratio. The peaks of the fragment ions III which lost 28 mass units (CO) from II were observed for Mn, Co, Ni, Cu, and Pd chelates. In order to study the stability of metal chelates against electron impact, special attention was paid to the peaks of I and II, which are supposed to be affected strongly by the *d*-electron number, electronegativity, ionization potential, and the ionic radius of central metal atoms. The intensity ratios of peaks I to II were obtained in the order Zn>Ni>Pd≈Co>Mn>Cu>Pb. It has been shown that the intensity ratios are related to the charge-radius ratio (e/r) of central metal atoms and the stability constants ($\log k_2$) of oxine metal chelates.

Studies have been carried out on metal chelates of acetylacetone and its derivatives by mass spectrometry.[2] With respect to the metal chelates of 8-quinolinol (oxine) and its derivatives, Jenkins *et al.* reported on the determination of metal purity in the order of 10^{-12} g as a form of oxine metal chelate by mass spectrometry.[3] Charalambous *et al.* recently reported on the fragmentation of oxine chelates with trivalent metals.[4] Budzikiewicz *et al.* found that fragmentation of the side chain in 2-*n*-butyloxine chelates was affected by their central metal atoms.[5] Although studies on mass spectrometry have been carried out to confirm the molecular weight of the metal complexes isolated,[6] no investigation has been made from the viewpoint of coordination chemistry. We have thus investigated mass spectrometry of oxine metal chelates in order to examine the stability of metal chelates against electron impact.

Results and Discussion

Mass spectra of divalent metal oxinates are shown in Fig. 1.

The fragmentation sequences are summarized in Chart 1. A peak of the molecular ion ($M^{\ddagger}$, I) appeared in the highest portion of the mass number of each metal chelate, attributable to the chelates in a 2: 1 ratio. A loss of 144 mass units was observed in each spectrum in common. This may be explained by the loss of one molecule of the coordinated oxine from I, affording fragment ion II of a 1: 1 complex. The peaks of III produced by the loss of 28 mass units from II are observed for Mn, Co, Ni, Cu, and Pd chelates. This can be explained by the loss of CO since the metastable ion peaks are observed distinctly in these spectra (ex. Ni(oxine)$_2$; m/e 202→174, calcd 149.8812, found 150.0). However, the peak of fragment ion III has not been detected for both Zn and Pb chelates. A plausible explanation for the lack of ion III in the mass spectra of both Zn and Pb chelates is that ion IV is directly produced from ion II, ion III being skipped, but the reason why the fragmentation schemes of these two chelate compounds are different from other chelates has not yet been clarified.

No peak at m/e 144 due to the oxinate ion was observed in almost all the chelates, that at m/e 145 (oxine ion) being found instead. (A similar phenomenon was

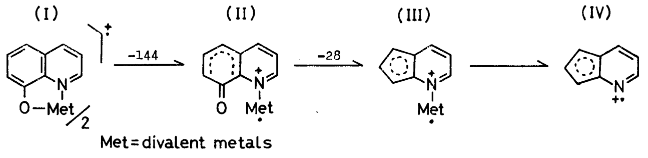

Chart 1. Fragmentation sequences of divalent metal oxinates.

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[3] A. E. Jenkins, J. R. Majer, and M. J. A. Reade, *Talanta*, **14**, 1213 (1967).

[4] J. Charalambous, M. J. Frazer, R. K. Lee, A. H. Qureshi, and F. B. Taylor, *Org. Mass Spectrom.*, **5**, 1169 (1971).

[5] H. Budzikiewicz and E. Plöger, *ibid.*, **3**, 709 (1970).

[6] P. R. Scherer and Q. Fernando, *Anal. Chem.*, **40**, 1938 (1968).

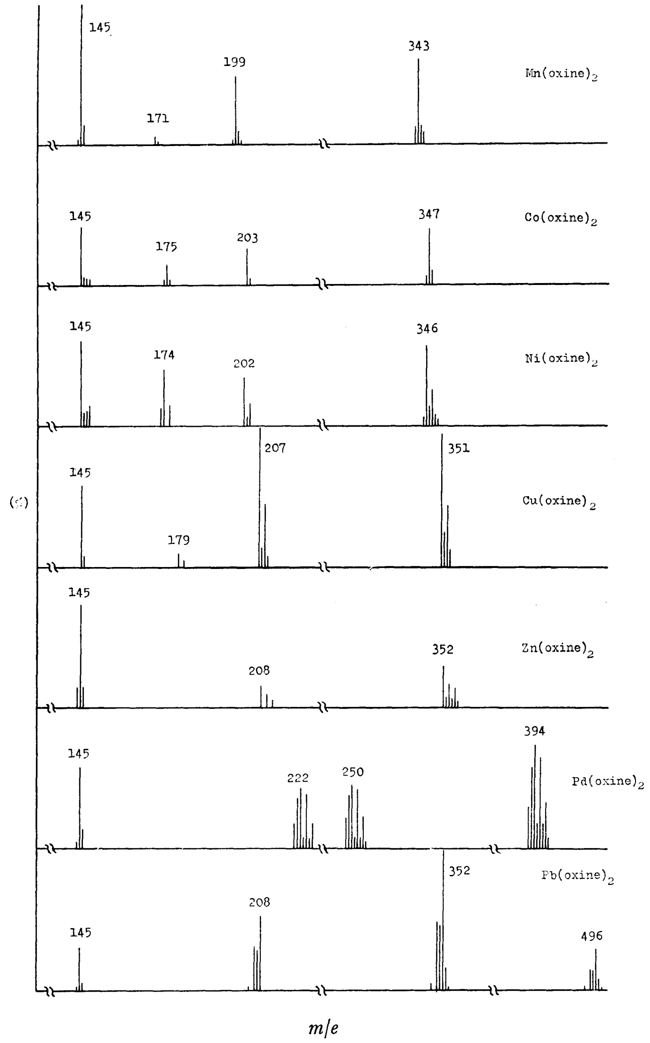

Fig. 1. Mass spectra of divalent metal oxinates
(*m/e* values are given for the ions containing ^{58}Ni, ^{63}Cu, ^{64}Zn, ^{106}Pd, and ^{208}Pb).

also observed in the mass spectra of acetylacetone metal chelates; no peak at *m/e* 99, acetylacetonate ion, but one at *m/e* 100, acetylacetone ion, being found.[2]) This can be explained as follows: (a) the peak at *m/e* 144 is afforded by the production of the oxinate ion, but it is very unstable and does not reach the ion collector in the mass spectrometer, (b) the peak at *m/e* 145 can be attributed to the oxine, whose oxinate ion produced from I may pick up one hydrogen atom affording the peak at *m/e* 145. However, in this experiment, the sample was introduced by a direct inlet system, being the little possibility for a hydrogen atom to be picked up in the mass spectrometer. The peak at *m/e* 145 is regarded to arise from the oxine molecule produced by thermal decomposition prior to the vaporization of sample. Charles studied the differential thermal analyses of oxine metal chelates and reported that the heat stability at melting point was in the order Cu>Pb>Zn>Ni>Co>Mn>Mg.[7] The intensity ratio of the peak at *m/e* 145 to I were therefore obtained, since the peak of I was supposed to be unaffected by thermal decomposition. The order of the ratios is Mg>Zn>Mn>Co>Ni>Pb>Cu, coinciding well with the heat instability order by Charles, since the peak at *m/e* 145 was considered to be due to the oxine molecule produced by thermal decomposition.

In order to compare the stability of metal chelates against electron impact, special attention was paid to the relationship between ions I and II, both of which might be affected strongly by the *d*-electron number, electronegativity, ionization potential and ionic radius of central metal atoms. In order to find the stability of ion I of the chelates with various metals, the intensity ratios of the peaks were substituted into formula I/(I+II), the stability of the molecular ions against electron impact being found to be in the order Zn> Ni>Pd≈Co>Mn>Cu>Pb (Table 1).

TABLE 1. INTENSITY RATIOS OF THE MOLECULAR ION, I, TO THE FRAGMENT ION, II

	Zn	Ni	Pd	Co	Mn	Cu	Pb
I/(I+II)%	67	63	61	61	55	48	22

By plotting the values of the intensity ratio against the charge-radius ratio (*e/r*),[8] a linear relationship was obtained (Fig. 2). It was found that the greater the charge-radius ratio of metal atoms, the higher the stability of ion I.

The correlation between the stability constants of oxine metal chelates in solution[9] and the stabilities to electron impact is given in Fig. 3. The process which produced ion II from I may be understood in relation

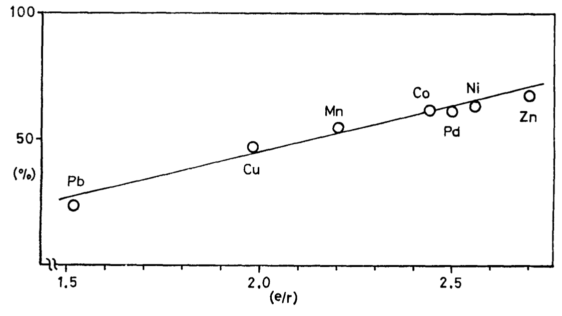

Fig. 2. Correlation between the stability upon electron impact and the charge-radius ratio.

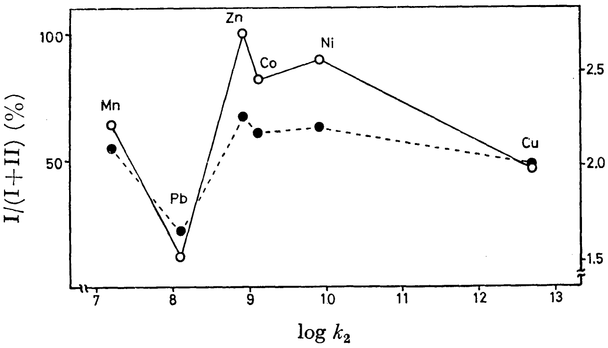

Fig. 3. Plots of intensity ratio and charge-radius ratio against stability constant log k_2.
---●--- Intensity ratio, —○— Charge-radius ratio.

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[7] R. G. Charles, *Anal. Chim. Acta*, **27**, 474 (1962).

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

[9] Stability constants were taken from: W. D. Johnston and H. Freiser, *J. Amer. Chem. Soc.*, **74**, 5239 (1952).

to the step of the second stability constant ($\log k_2$). From the plot intensity ratio *vs.* $\log k_2$, (broken line) we see that there is a correlation between the stability constant and the charge-radius ratio, showing a linear relationship for the stability of ion I, against electron impact. A similar, plot e/r *vs.* $\log k_2$ (solid line) is given. The plots are similar in form, indicating that intensity ratio is correlated to stability constant.

In conclusion, the binding ratios of the ligands to metals can be easily determined by measurements of the mass spectra of metal chelates with a trace amount of the sample. Helpful information can be obtained for the stability of metal chelates against electron impact.

Experimental

Mass spectra were measured by a Hitachi RMU-7 mass spectrometer according to a direct inlet system under the following conditions: ionizing voltage 70 eV, ion accelerating voltage 1800 V, total emission current 80 μA, ion source temperature 250 °C. Metal oxinates were prepared by the usual method,[10] their purity being confirmed by elemental analyses.

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