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# MASS SPECTROMETRY OF DIVALENT METAL OXINATES

Yoshinori KIDANI, Shinobu NAGA, and Hisashi KOIKE
Faculty of Pharmaceutical Sciences, Nagoya City University
Mizuho-ku, Nagoya, Japan

In order to apply mass spectrometry to metal complex chemistry, the mass spectra of oxinates of divalent metals (Zn, Cu, Ni, Co and Mn) were measured and the fragmentation of oxinates were investigated.

It was found that there are two types of decomposition pathways, and the ionic radii of the metals were found to be related closely to the mass intensity ratio between the molecular ion and the fragment ion of 1 : 1 complex ( $M^{\dagger}$ - 144 ). The stabilities of metal oxinates against electron impact have been considered.

A. E. Jenkins$^{1)}$ reported on the detection of a tracer amount, $10^{-12}$ g. of metals with oxine by mass spectrometry, and H. Budzikiewicz et al.$^{2)}$ studied on the fragmentation of the side chain of metal 2-n-butyloxinates. Besides these studies, mass spectrometry has been employed for the measurements of molecular weights of metal complex. However, any mass spectrometric studies of metal chelates of oxine derivatives$^{*)}$ have not been carried out so far.

In order to apply mass spectrometry to the studies of metal complexes, the authors, attempted mass spectrometric measurements of divalent metal oxinates of Zn, Cu, Ni, Co and Mn with a Hitachi RMU - 7 type, double focusing mass spectrometer. Metal oxinates have not been considered to be measurable because of their lower vapor pressure, though the mass spectrum and the fragmentation of ligand, oxine, was reported by D. M. Clugston$^{3)}$.

Metal oxinates decompose initially to give the peak at $M^{\dagger}$-144 (II) ; this is considered to be due to the loss of one coordinated ligand from the molecular ion (I) of 2 : 1 complex, leading to the fragment ion of 1 : 1 complex, shown in Fig. 1 and Chart 1. By the subsequent loss of 28 mass units of CO from the fragment ion (II), almost all oxinates afforded the ions at m/e 116 (IV), following the pathway through the intermediate ion $M^{\dagger}$-144-28 (III). However, in the case of Zn oxinate, the fragment ion (III) was not observed in the spectrum. This fact may be explained by assuming that the fragment ion (III) of the other metal complexes is stable, to a certain extent, whereas that of Zn is rather so unstable that it was not observed. Almost all oxinates decompose to the ion (IV) through the pathway of the route A, whereas it seems that Zn oxinate may be decomposed to the ion (IV) directly through the pathway of the route B, as is

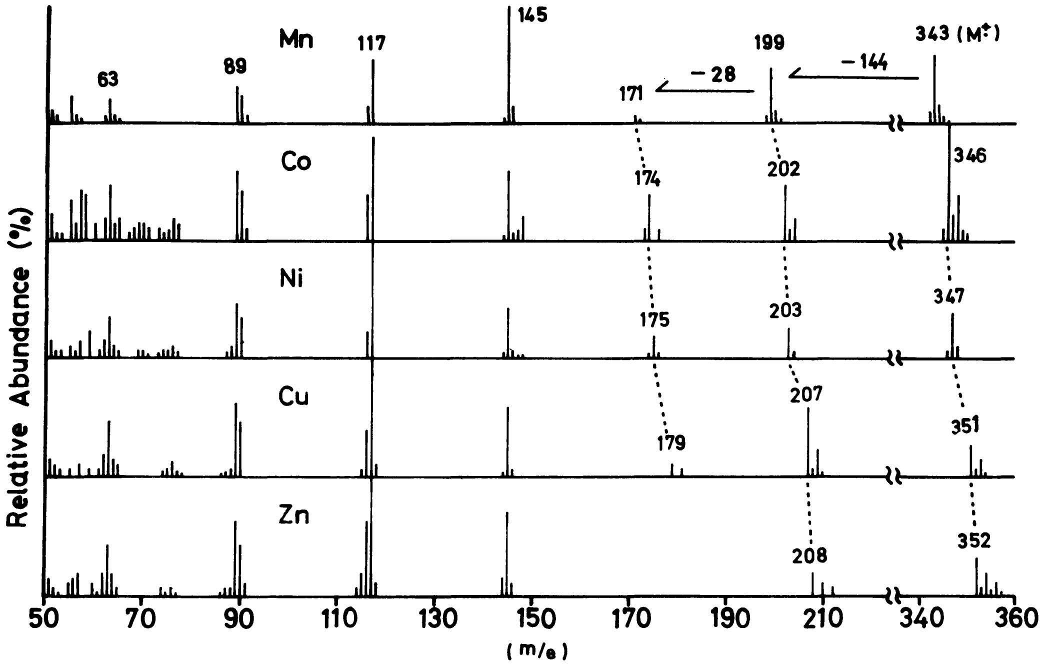

Figure 1. Mass spectra of various divalent metal oxinates.

Sample introduction ; Direct inlet system.
Ionizing voltage ; 70 eV.
Ion accelerating voltage ; 1800 V.
Total emission current ; 80 μA.
Ion source temperature ; 250° C.
Sample heating temperature ; 140 ~ 200° C

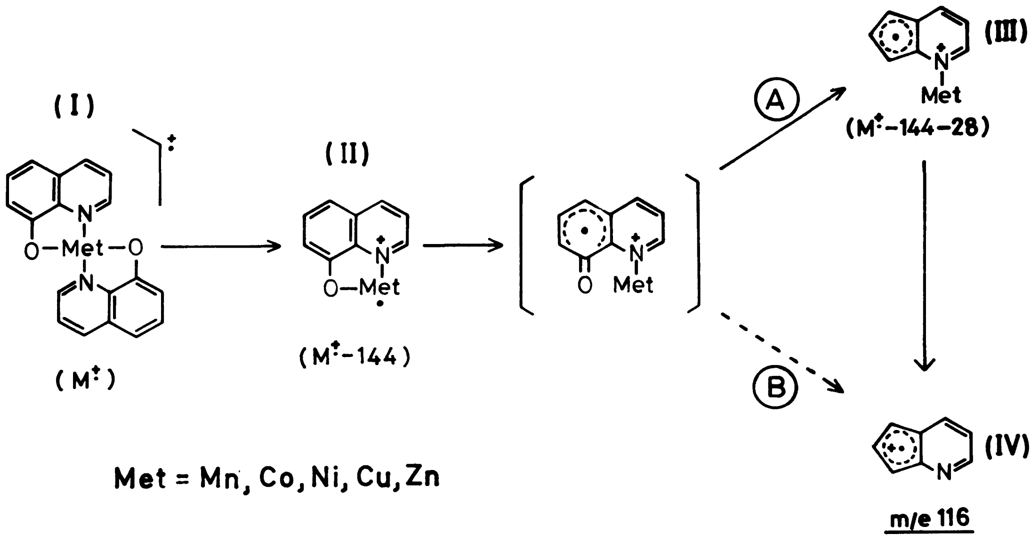

Chart 1. Fragmentations of divalent metal oxinates.

shown in Chart 1, owing to the instability of the fragment ion (III) of Zn.

In order to compare the stabilities of metal oxinates against electron impact, the correlation between the ionic radii[4)] and the intensity ratios of the molecular ions and the fragment ions (II), shown in Table 1, was examined and it was found that a very close relationship exists between them, as is shown in Fig. 2. It is indicated that the larger the ionic radius, the smaller the stability of oxinate against electron impact.

By mass analyses, the ligand : metal molar ratios of the complexes are easily learned to be 2 : 1 in the divalent metal complexes used.

Table 1. Intensity ratios between the molecular ion, I (2:1 ratio complex) and the fragment ion, II (1:1 ratio complex).

| | $M^{+}$ | $M^{+}-144$ | $\frac{M^{+}-144}{M^{+}+(M^{+}-144)}$ (%) |
|---|---|---|---|
| Mn | 60 | 49 | 45 |
| Co | 40 | 26 | 39 |
| Ni | 100 | 46 | 32 |
| Cu | 30 | 59 | 66 |
| Zn | 31 | 15 | 33 |

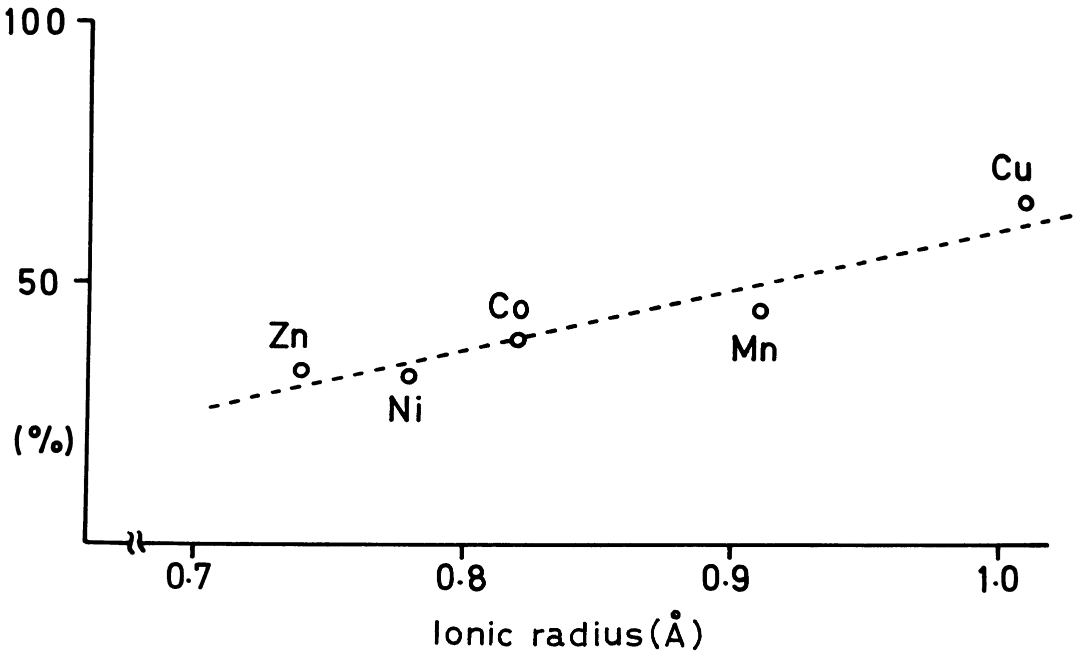

Figure 2. Correlation between ionic radius and intensity ratio.

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## References

1) A.E.Jenkins, J.R.Majer and M.J.A.Reade, Talanta, 14 , 1213(1967).
2) H.Budzikiewicz and E.Plöger, Org. Mass Spectrom., 3 , 709(1970).
3) D.M.Clugston and D.B.MacLean, Can. J. Chem., 44 , 781(1966).
4) Joyo Kagaku Binran Hensyu Iinkai, "Joyo Kagaku Binran", Seibundoshinkosha, Tokyo, 1960, p.630.
*) Very recently we learned that mass spectroscopy of metal oxinates with trivalent metals was reported ( J. Charalambous, M. J. Frazer, R. K. Lee, A. H. Qureshi and F. B. Taylor, Org. Mass Spectrom., 5 , 1169(1971) ).

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