Studies on Mass Spectrometry of Metal Chelates. IV. Synthesis and Mass Spectrometry of Cobalt(III) Mixed Ligand Chelates

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The ligand substitution reaction of $Co(acac)_3$ proceeded with other ligands L (L=oxine, 2-Me-oxine, 4-Me-oxine, 5-Me-oxine, and 7-Me-oxine), to afford mixed ligand chelates, $Co(acac)_2(L)$ and $Co(acac)(L)_2$. Their mass spectra gave the following fragmentation patterns. The $Co(acac)_2(L)$ type chelate gave a fragment ion Co(acac)(L), produced by the loss of one molecule of acac from the molecular ion. At the same time it produced another fragment ion, $Co(acac)_2$, by the loss of L from the molecular ion. From this fragmentation pattern it was confirmed that the compound is a mixed ligand chelate having the binding ratio Co: acac: L=1: 2: 1. The $Co(acac)(L)_2$ type chelate produced a fragment ion, Co(acac)(L), by the loss of one molecule of L from the molecular ion, and another fragment ion of $Co(L)_2$ by the loss of acac from the molecular ion. From this fragmentation pattern it was confirmed that the compound is another mixed ligand chelate having the binding ratio Co: acac: L=1: 1: 2.

In order to apply mass spectrometry to the investigation of metal chelates, the authors reported on the mass spectrometric studies of the divalent metal chelates of 8-quinolinol (oxine),[1] 8-quinolinethiol (thiooxine),[2] 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).[3] As a part of this study, the authors attempted to apply mass spectrometry to the mixed ligand chelates. Cobalt(III) mixed ligand chelates with 2,4-pentanedione (acac) and oxine,[4] 2-, 4-, 5-, and 7-Me-oxine were newly synthesized, and analyses of their mass spectra, thin layer chromatogram and infrared absorption spectra were made. In this paper, syntheses of two types of Co(III) mixed ligand chelate with acac and oxine and its mono-methyl derivatives are described. From identification of the mixed ligand chelate formation by thin layer chromatography, infrared absorption spectral analyses and elementary analyses, mass spectrometry has been carried out, the fragmentations mainly being discussed. No investigation of the application of mass spectrometry to mixed ligand chelates seems to have been reported yet. The present studies suggest that mass spectrometry could well be applied to the identification of mixed ligand chelate formation and also to the determination of a binding ratio of ligand to metal.

Results and Discussion

Syntheses of Mixed Ligand Chelates. Various mixed ligand chelates were newly synthesized by means of ligand substitution reactions of tris(acetylacetonato) cobalt(III), $Co(acac)_3$, with oxine, 2-, 4-, 5-, and 7-Me-oxine. The reaction products were separated by means of column chromatography into four fractions a, b, c, and d as follows: Ia—Id for oxine, IIa—IId for 2-Me-oxine, IIIa—IIId for 4-Me-oxine, IVa—IVd for 5-Me-oxine, and Va—Vd for 7-Me-oxine.

Thin Layer Chromatography. Four fractions of five oxine derivatives. The twenty fractions separated by column chromatography were identified in comparison with thin layer chromatography of the parent metal chelates, $Co(acac)_3$, $Co(oxine)_3$, and $Co(mono\text{-}Me\text{-}oxine)_3$ (Table 1). It was confirmed that Ia, IIa, IIIa, IVa, and Va have the same R_f value as $Co(acac)_3$; Id, IId, IIId, IVd, and Vd have the same R_f value as $Co(oxine)_3$, $Co(2\text{-}Me\text{-}oxine)_3$, $Co(4\text{-}Me\text{-}oxine)_3$, $Co(5\text{-}Me\text{-}oxine)_3$, and $Co(7\text{-}Me\text{-}oxine)_3$, respectively. On the other hand, b and c fractions of I—V show characteristic R_f values, quite different from the corresponding parent metal chelates, suggesting the production of mixed ligand chelates.

Infrared Absorption Spectra. Infrared (IR) absorption spectra were measured (4000—400 cm^{-1}) by means of the KBr disc method. Infrared absorption spectra of fraction a of I—V coincided with the spectrum of $Co(acac)_3$, while fraction d of I—V gave the same IR spectra as those of $Co(oxine)_3$, $Co(2\text{-}Me\text{-}oxine)_3$, $Co(4\text{-}Me\text{-}oxine)_3$, $Co(5\text{-}Me\text{-}oxine)_3$, and $Co(7\text{-}Me\text{-}oxine)_3$, respectively. On the other hand, similar spectra were shown for Ib and Ic, IIb and IIc, IIIb and IIIc, IVb and IVc, and Vb and Vc. In addition they have characteristic absorption bands of the corresponding parent metal chelates. It thus appears that fractions b and c of I—V possess acetylacetone and either oxine or mono-Me-oxine. From a detailed investigation of the spectra between fractions Ib and Ic, it was found that in the IR spectrum of Ib the intensity of the absorption band at 1513 cm^{-1} (assignable to the C=O stretch-

TABLE 1. R_f VALUES OF MIXED LIGAND CHELATES ON THIN LAYER CHROMATOGRAM

Oxine	Ia (0.63)	Ib (0.25)	Ic (0.30)	Id (0.12)
2-Me-oxine	IIa (0.65)	IIb (0.21)	IIc (0.18)	IId (0.10)
4-Me-oxine	IIIa (0.63)	IIIb (0.29)	IIIc (0.35)	IIId (0.16)
5-Me-oxine	IVa (0.64)	IVb (0.25)	IVc (0.28)	IVd (0.16)
7-Me-oxine	Va (0.65)	Vb (0.31)	Vc (0.36)	Vd (0.30)

R_f values of parental metal chelates

$Co(acac)_3$=0.64 $Co(oxine)_3$=0.12

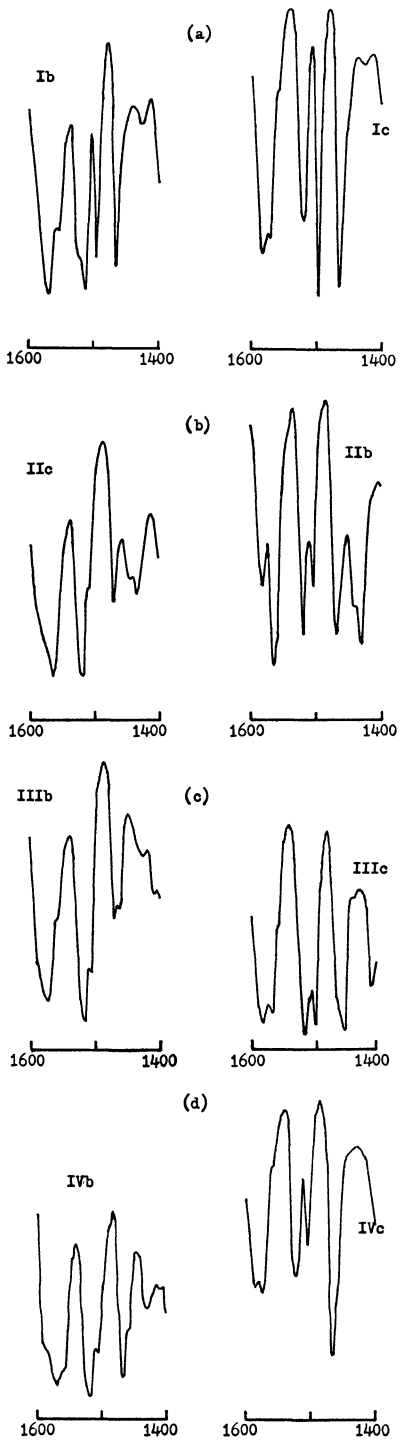
$Co(2\text{-}Me\text{-}oxine)_3$=0.11 $Co(4\text{-}Me\text{-}oxine)_3$=0.17

$Co(5\text{-}Me\text{-}oxine)_3$=0.16 $Co(7\text{-}Me\text{-}oxine)_3$=0.31

adsorbent; Kieselgel H nach Stahl, 0.25 mm.

developer; benzene: methanol=95: 5 v/v.

ing vibration of $Co(acac)_3$[5]) is stronger than that at 1496 cm^{-1} (assignable to the quinoline ring vibration[6]), but in that of Ic the intensity of the absorption band at 1497 cm^{-1} is stronger than that at 1520 cm^{-1} (Fig. 1-a). In the IR spectra of IIc, IIIb, IVb, and Vb, absorption bands at 1505 cm^{-1} assignable to the quinoline ring vibration are observed as a shoulder, while in those of IIb, IIIc, IVc, and Vc absorption bands with medium strength are observed (Fig. 1-b, c, d, and e). The fractions can be classified into two groups, (1) in which the quinoline ring vibration band is of low intensity (Ib, IIc, IIIb, IVb, and Vb), and (2) in which it is of high intensity (Ic, IIb, IIIc, IVc, and Vc). It appears that the ligand substitution reaction of $Co(acac)_3$ takes place with the stepwise substitution of the acac ion in $Co(acac)_3$ with the other ligand. It is thus presumed that group (1) includes the mixed ligand chelates produced by the substitution of one acac ion in $Co(acac)_3$ with the other ligand, and group (2) the chelate produced by the substitution of two acac ions in $Co(acac)_3$ with the other ligands.



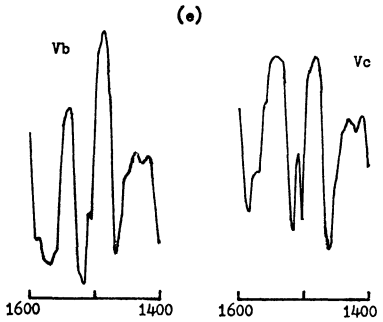


Fig. 1. IR spectra of mixed ligand chelates.
Ib; $Co(acac)_2(oxine)$, Ic; $Co(acac)(oxine)_2$, IIb; $Co(acac)(2\text{-Me-oxine})_2$ IIc; $Co(acac)_2(2\text{-Me-oxine})$, IIIb; $Co(acac)_2(4\text{-Me-oxine})$, IIIc; $Co(acac)(4\text{-Me-oxine})_2$, IVb; $Co(acac)_2(5\text{-Me-oxine})$, IVc; $Co(acac)(5\text{-Me-oxine})_2$, Vb; $Co(acac)_2(7\text{-Me-oxine})$, Vc; $Co(acac)(7\text{-Me-oxine})_2$.

Elementary analyses of these mixed ligand chelates coincided well with the theoretical values as shown in Table 2.

Mass Spectra. Mass spectra of compounds Ib and Ic, inferred from their IR spectra, are shown in Fig. 2. They are seen to have compositions $Co(acac)_2$-(oxine) and $Co(acac)(oxine)_2$, respectively. In the

Table 2. Elementary analyses of mixed ligand chelates

Compound	Analyses (%) Calcd (Found)		
	C	H	N
Ib; $Co(acac)_2(oxine)$	56.87 (57.08	5.02 5.17	3.49 3.48)
Ic; $Co(acac)(oxine)_2$	61.88 (61.49	4.26 4.55	6.28 6.16)
IIb; $Co(acac)(2\text{-Me-oxine})_2$	63.30 (63.40	4.89 5.05	5.90 6.35)
IIc; $Co(acac)_2(2\text{-Me-oxine})$	57.84 (58.01	5.34 5.31	3.37 3.31)
IIIb; $Co(acac)_2(4\text{-Me-oxine})$	57.84 (57.78	5.34 5.61	3.37 3.53)
IIIc; $Co(acac)(4\text{-Me-oxine})_2$	63.30 (63.32	4.89 5.01	5.90 5.50)
IVb; $Co(acac)_2(5\text{-Me-oxine})$	57.84 (57.81	5.34 5.30	3.37 3.29)
IVc; $Co(acac)(5\text{-Me-oxine})_2$	63.30 (63.57	4.89 5.15	5.90 5.70)
Vb; $Co(acac)_2(7\text{-Me-oxine})$	57.84 (57.89	5.34 5.47	3.37 3.35)
Vc; $Co(acac)(7\text{-Me-oxine})_2$	63.30 (63.30	4.89 4.99	5.90 5.85)

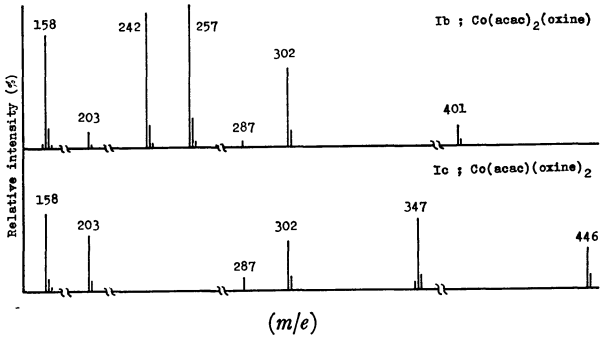


Fig. 2. Mass spectra of $Co(acac)_2(oxine)$ and $Co(acac)(oxine)_2$.

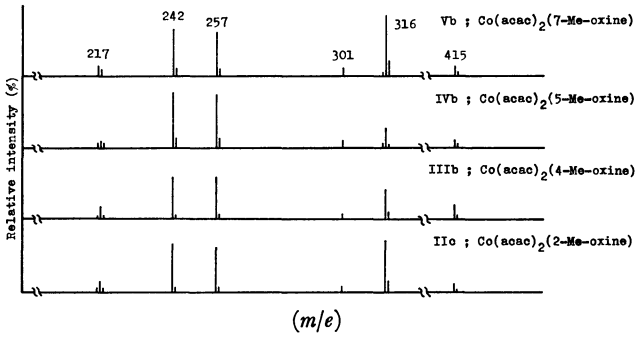
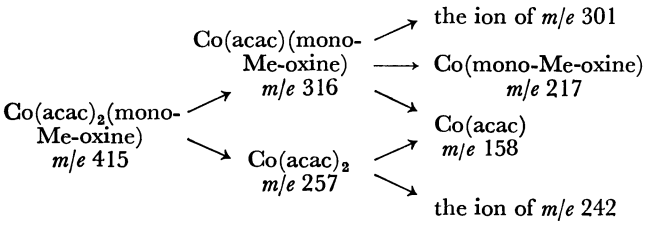


Fig. 3. Mass spectra of $Co(acac)_2$(2-Me-oxine), $Co(acac)_2$(4-Me-oxine), $Co(acac)_2$(5-Me-oxine), and $Co(acac)_2$(7-Me-oxine).

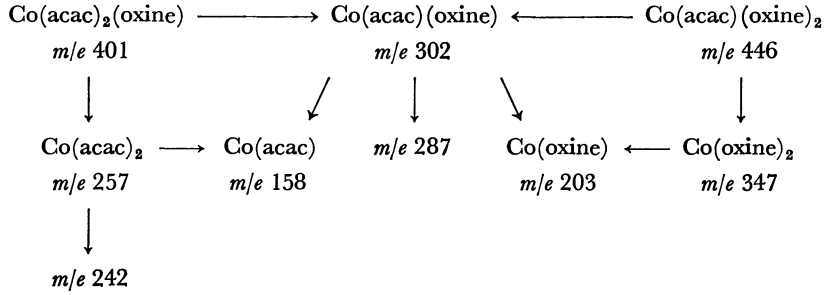
highest mass region of their spectra, the peak appears at *m/e* 401 and 446, respectively, which correspond to the respective molecular weight of the inferred mixed ligand chelates. Peaks at *m/e* 302, 287, 203, and 158 are commonly observed in both spectra. The peak at *m/e* 302 appears with a difference of 99 amu from *m/e* 401 and 144 amu from *m/e* 446. The peak at *m/e* 203 appears with a difference of 99 amu from the peak at *m/e* 302, and that at *m/e* 158 with a difference of 144 amu from the peak at *m/e* 302. The 99 amu corresponds to one molecule of acac, while the 144 amu corresponds to one molecule of oxine. Consequently, it appears that the fragment ion of *m/e* 302 has a 1: 1: 1 ratio of Co: acac: oxine, and the fragment ions of *m/e* 203 and 158 have a 1: 1 ratio of Co: oxine and Co: acac, respectively. It seems that the ion of *m/e* 287 is produced by the loss of $CH_3\cdot$ from the ion of *m/e* 302. Two peaks at *m/e* 257 and 242 are observed only in the spectrum of $Co(acac)_2(oxine)$, and they correspond to the difference between the molecular ion peak (*m/e* 401) and 144 or 144+15 amu. Accordingly, the ion of *m/e* 257 has the composition $Co(acac)_2$, while that of *m/e* 242 is produced by the loss of $CH_3\cdot$ from the ion of *m/e* 257. Since the peak at *m/e* 347 observed only in the spectrum of $Co(acac)(oxine)_2$ corresponds to the molecular ion peak (*m/e* 446) minus 99 amu, it appears that the ion has the composition $Co(oxine)_2$. The fragmentation pathways of these mixed ligand chelates are shown in Scheme 1. Based on these fragmentation patterns, the compounds were identified as the mixed ligand chelates having a 1: 2: 1 and 1: 1: 2 binding ratio of Co: acac: oxine.

Figure 3 shows mass spectra of the compounds inferred to have respective compositions $Co(acac)_2$(2-Me-oxine), $Co(acac)_2$(4-Me-oxine), $Co(acac)_2$(5-Me-oxine), and $Co(acac)_2$(7-Me-oxine). Each has a peak in the highest mass region at *m/e* 415, which corresponds to the molecular weight of the assumed compound. In the mass range lower than *m/e* 415, major peaks were observed at *m/e* 316, 301, 257, 242, 217, and 158. It appears that these peaks originate in the ion produced according to the fragmentation pathway shown in Scheme 2. The fragment ion of *m/e* 316 with the composition Co(acac)(mono-Me-oxine) is produced by the loss of one molecule of acac from the molecular ion (*m/e* 415). On the other hand, the fragment ion of *m/e* 257 with the composition $Co(acac)_2$ is produced by the loss of mono-Me-oxine (158 amu) from the molecular ion. Other fragment ions of *m/e* 158 and 217 are produced by the loss of acac and mono-Me-oxine from the ion of *m/e* 316, respectively. It seems that the ion of *m/e* 301 is produced by the loss of $CH_3\cdot$ from the ion of *m/e* 316. Based on this fragmentation pattern, it has been confirmed that these mixed ligand chelates have a 1: 2: 1 binding ratio of Co: acac: mono-Me-oxine.

Fugure 4 shows mass spectra of the compounds assumed to have respective compositions Co(acac)(2-Me-oxine)$_2$, Co(acac)(4-Me-oxine)$_2$, Co(acac)(5-Me-oxine)$_2$, and Co(acac)(7-Me-oxine)$_2$. The spectra of



Scheme 2. Fragmentation of $Co(acac)_2$(mono-Me-oxine) type mixed ligand chelate.



Scheme 1. Fragmentation of mixed ligand chelates, $Co(acac)_2(oxine)$ and $Co(acac)(oxine)_2$.

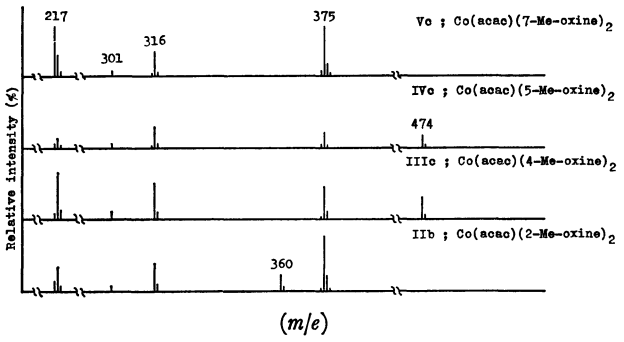
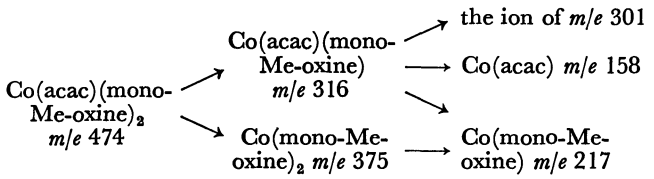


Fig. 4. Mass spectra of Co(acac)(2-Me-oxine)$_2$, Co(acac)-(4-Me-oxine)$_2$, Co(acac)(5-Me-oxine)$_2$, and Co(acac)-(7-Me-oxine)$_2$.

both Co(acac)(4-Me-oxine)$_2$ and Co(acac)(5-Me-oxine)$_2$ have a peak at *m/e* 474 in the highest mass region, corresponding to the molecular weight of the assumed compound, but the spectra of Co(acac)(2-Me-oxine)$_2$ and Co(acac)(7-Me-oxine)$_2$ do not give a molecular ion peak at *m/e* 474. The reason for its absence is explained by the fact that the two mixed ligand chelates have two molecules of 2-Me-oxine or 7-Me-oxine and therefore the chelates are liable to undergo steric hindrance. Thus, it may be difficult for the molecular ion produced by electron impact to exist stably. Since the peak at *m/e* 375 observed in each spectrum corresponds to the fragment ion with a difference of 99 amu (one molecule of acac) from the molecular ion peak, it appears that the peak at *m/e* 375 is a fragment ion having the composition Co(mono-Me-oxine)$_2$. The peak at *m/e* 360 can only be observed in the spectrum of Co(acac)(2-Me-oxine)$_2$. This corresponds to the ion produced by the loss of $CH_3\cdot$ from the ion of *m/e* 375, and the fragmentation pattern coincides with that of Co(2-Me-oxine)$_2$ already described by the authors.[3] The peak at *m/e* 316 appears with a difference of 158 amu (corresponding to one molecule of mono-Me-oxine) and is also observed in the spectrum of Co(acac)$_2$(mono-Me-oxine). Thus it is the peak corresponding to the fragment ion having the composition Co(acac)(mono-Me-oxine). The fragmentation pattern is shown in Scheme 3. Based on this fragmentation pattern, it has been confirmed that these mixed ligand chelates have a 1:1:2 binding ratio in Co: acac: mono-Me-oxine.

It may be suspected that each of these chelates containing either 2- or 7-Me-oxine is a mixture of Co(acac)-(mono-Me-oxine) and Co(mono-Me-oxine)$_2$, since no molecular ion peak was observed at *m/e* 474. However, the authors confirmed that all the compounds synthesized and used for the measurement of mass spectra are completely pure single substance by identification



Scheme 3. Fragmentation of Co(acac)(mono-Me-oxine)$_2$ type mixed ligand chelate.

of thin layer chromatography and elementary analyses as is shown in Table 2. Based on these facts, it seems that the spectra are not those of a mixture of Co(acac)-(mono-Me-oxine) and Co(mono-Me-oxine)$_2$.

Experimental

Reagents. Co(acac)$_3$, oxine, and 2-Me-oxine of special grade regents were used without further purification. 4-Me-oxine,[7] 5-Me-oxine,[8] and 7-Me-oxine[8] were synthesized by the reported methods. Kieselgel 60, Merck Co., and Activated Alumina, Wako Pure Chemicals Co., were used as adsorbent for column chromatography. Kieselgel H nach Stahl, Merck Co., was used as adsorbent for thin layer chromatography.

Apparatus. IR spectra were measured with a Nihon Bunko JASCO IRA-2 by means of the KBr disc method. Mass spectra were measured with a Hitachi RMU-7 mass spectrometer by introducing the samples through a direct inlet system. The other conditions were as follows; ionizing voltage 70 eV, ion accelerating voltage 1800 V, total emission current 80 μA, ion source temperature 250 °C, and sample evaporating temperature 110—240 °C.

Thin Layer Chromatography. Thin layer chromatography was carried out on plates of 0.25 mm thickness, which were activated at 110 °C for 1 hr. The solvent mixture used was benzene: methanol=95:5 v/v.

Synthesis. Tris(acetylacetonato) cobalt (III) and oxine or its methyl derivatives are dissolved in either water, methanol, or a mixed solvent of acetone and methanol and this solution in the presence of active charcoal is refluxed on a water bath. After a few minutes, the charcoal is filtered off while hot and the residue is washed well with chloroform. This washing is combined to the preceding filtrate and the solution is concentrated under reduced pressure. The concentrate thus obtained was separated by column chromatography with silica gel or alumina (eluent; chloroform or benzene).

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