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MASS SPECTROMETRY OF COBALT(III) MIXED LIGAND CHELATES WITH ACETYLACETONE AND OXINE

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Two kinds of Co(III) mixed ligand chelates with acetylacetone and oxine were newly synthesized, and their mass spectra were analyzed. A binding ratio of Co, acac, and oxine has been determined to be 1 : 2 : 1 and 1 : 1 : 2 respectively, and it was found that $Co(acac)(oxine)_2$ was more stable than $Co(acac)_2(oxine)$ under electron impact.

In a series of mass spectrometric studies of metal chelates, the authors attempted to apply mass spectrometry to the identification of mixed ligand chelates. The mass spectrometric studies of acac chelates were reported, [1] and the authors studied on the mass spectroscopy of oxine chelates. [2] For this purpose, Co(III)-acac-oxine mixed ligand chelates were newly prepared. In this paper, mass spectral analysis of $Co(acac)_2(oxine)$ and $Co(acac)(oxine)_2$ were discussed.

Two kinds of mixed ligand chelates were synthesized by reacting $Co(acac)_3$ with oxine in water in the presence of active charcoal. The reaction mixture was seperated by means of column chromatography with silica gel (eluent ; $CHCl_3$) into four fractions, Ia, Ib, Ic, and Id. These fractions were identified with thin layer chromatography (adsorbent ; Kieselgel H and developer ; benzene : methanol = 95 : 5 v/v). Ib (Rf = 0.25) and Ic (Rf = 0.30) snow individual characteristic Rf values, which are different from those of the parental metal chelates, Ia (Rf = 0.63) $Co(acac)_3$ and Id (Rf = 0.12) $Co(oxine)_3$, and therefore

they are considered to be the mixed ligand chelates expected.

Infrared absorption spectra were measured by means of the KBr disc method, and the spectra of both Ib and Ic were found to be quite similar to each other, possessing the characteristic absorption bands of both $Co(acac)_3$ and $Co(oxine)_3$. A comparative study of the spectra between Ib and Ic indicated that the intensity of the absorption band at 1513 cm^{-1}, which can be ascribed to the C=O stretching vibration [3] in the IR spectrum of Ib, was found to be stronger than that at 1496 cm^{-1}, which can be ascribed to the quinoline ring vibration. [4] However, in the IR spectrum of Ic, the intensity of the absorption band of the quinoline ring vibration at 1497 cm^{-1} is stronger than that of the C=O stretching vibration at 1520 cm^{-1}. Based on this fact, the authors presumed that the fraction Ib was $Co(acac)_2(oxine)$ and Ic was $Co(acac)(oxine)_2$.

Absorption maxima of the electronic absorption spectra of these mixed ligand chelates are listed in Table 1. It can be seen that both the mixed ligand chelates possess their parental absorption peaks, similarly to that of IR spectra.

Table 1. Visible and Ultraviolet Absorption Spectra (in 95 % ethanol)

Compound	λ_{max}, nm (log ε)				
$Co(acac)_3$	588(2.09)			255(4.94)	227(4.56)
$Co(oxine)_3$		403(3.97)	333(3.65)	251(4.94)	
Ib	544(2.23)	396(3.57)	322(3.85)	252(4.74)	226(4.72)
Ic	572(2.32)	395(3.86)	317(3.83)	252(4.88)	229(4.78)

Elementary analyses of Ib and Ic also indicated the mixed ligand chelate formation (shown in Table 2).

Table 2. Elementary Analyses of the Mixed Ligand Chelates

Compound		C	H	N
$Co(acac)_2(oxine)$	Calcd.	56.87	5.02	3.49
	Found	57.08	5.17	3.48
$Co(acac)(oxine)_2$	Calcd.	61.88	4.26	6.28
	Found	61.49	4.55	6.16

Mass spectra of Ib and Ic measured are shown in Fig.1. The peak of the higher mass region was observed at m/e 401 and 446, which corresponded to the molecular weight of $Co(acac)_2(oxine)$ and $Co(acac)(oxine)_2$, and they were considered to be the molecular ion peaks. A number of major peaks with lower m/e values were also observed. It seemed that those peaks are due to the ions

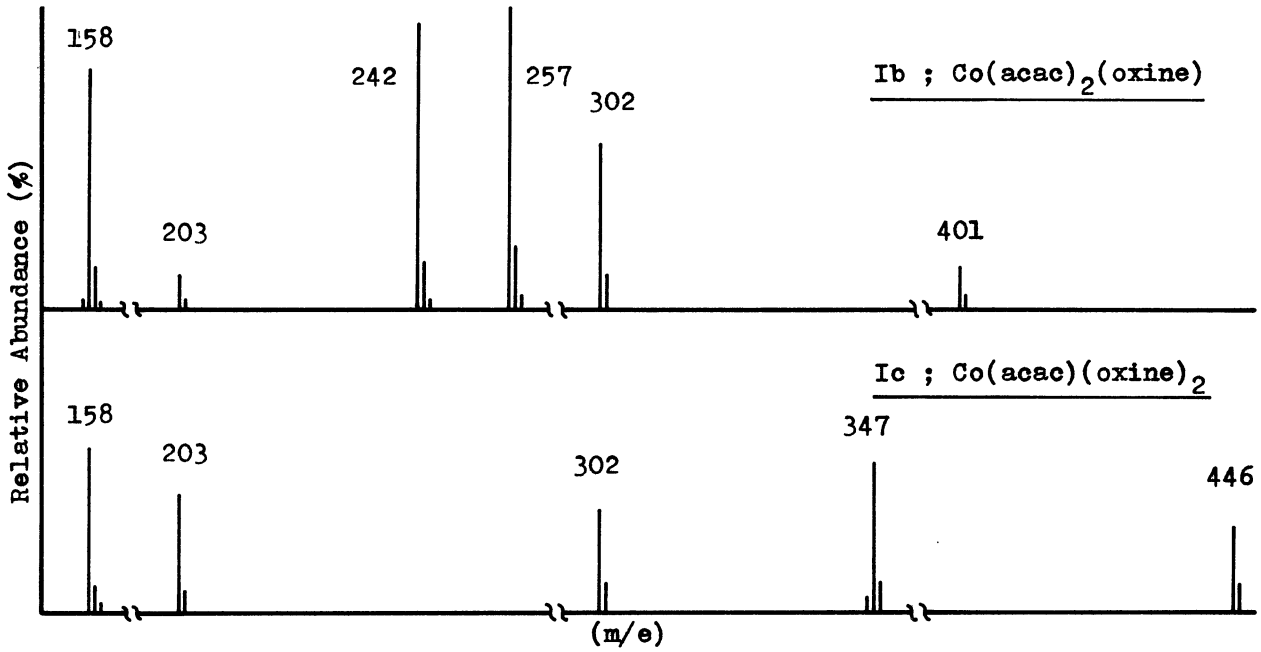
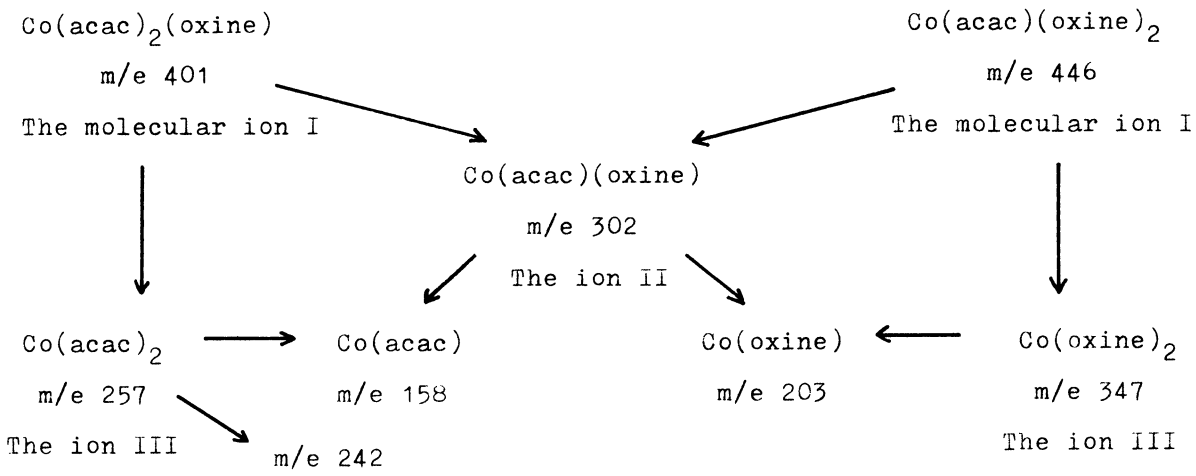


Fig. 1. Mass Spectra of $Co(acac)_2(oxine)$ and $Co(acac)(oxine)_2$

produced according to the fragmentation pathway shown in Scheme 1. The fragment ion, II, having a composition of Co(acac)(oxine) is produced by the loss of one molecule of coordinated acac (99 mass units) in the Ib, and of coordinated oxine (144 mass units) in the Ic. Simultaneously the other fragment ions having



Scheme 1. Fragmentation of $Co(acac)_2(oxine)$ and $Co(acac)(oxine)_2$

compositions of $Co(acac)_2$ and $Co(oxine)_2$ are produced respectively by the loss of coordinated oxine or acac from the molecular ions. Based on these fragmentation process, the compounds obtained can be identified as mixed ligand chelates of $Co(acac)_2(oxine)$ and $Co(acac)(oxine)_2$.

These mixed ligand chelates have two fragmentation pathways ; one is to give the fragment ion II and the other to afford the fragment ion III from the molecular ion I. Therefore, in order to compare the stabilities of the mixed ligand chelates under electron impact, an attention was paid on the relationship among the ions I, II, and III. In order to know the stabilities of the molecular ions, I, of the mixed ligand chelates under electron impact, the intensity ratios of the peaks were taken into consideration in the ratio of I/(I + II + III). As a result, the stability of the molecular ions under electron impact has been found to be $Co(acac)(oxine)_2 > Co(acac)_2(oxine)$ (shown in Table 3).

Table 3. Peak Intensity Ratios of the Mixed Ligand Chelates

	$Co(acac)(oxine)_2$	$Co(acac)_2(oxine)$
I/(I + II + III) %	26	19

These studies show that the mass spectrometry can be effectively applied to the identification of the mixed ligand chelate formation and also to the determination of the binding ratio of metal to ligands. Valuable information can also be obtained on the stability of mixed ligand chelates under electron impact.

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