Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. IX. Cobalt Complex Soap

By Hirotaro KAMBE*

(Received March 29, 1961)

It has been certified the cobalt soap is a salt between cobalt ion and fatty acid ion, in Part IV of these studies[1]. In the present paper, the preparation of soaps of cobalt complex ions is presented and some of their properties are investigated.

The reflection spectrum of cobalt complex soap shows that it certainly has color characteristics similar to those of the parent cobalt complex ion. In the infrared absorption spectrum, the existence of carboxylate ion is confirmed, as in simple cobalt soap. The magnetic susceptibility of complex soap verifies that cobalt(III) ion is in a state of an electronic configuration of d^2sp^3 six covalent complex ion. Decomposition at heating was followed by thermogravimetric analysis.

Experimental

Cobalt complex soaps were prepared by metathesis between inorganic cobalt complex salts and potassium soap, as was the simple cobalt soap described in Part I. Luteo-salt, $[Co(III)(NH_3)_6]Cl_3$, and purpureo-salt, $[Co(III)(NH_3)_5Cl]Cl_2$, were used as inorganic salts. Hereafter, these salts are called I and II respectively. Stearates of these complex ions are called I-S and II-S respectively.

Reflection spectrophotometry, infrared absorption spectrophotometry, and the measurement of magnetic susceptibility were carried out as in Parts III and IV. Thermogravimetry was conducted as in Part VI.

Results and Discussion

The reflection spectra of cobalt complex soaps are shown in Fig. 1, with that of inorganic complexes. Their trichromaticity constants were calculated as in Part III and are shown in Table I.

The similarity of the trichromaticity constants, in particular those of the dominant wavelength, of complex soaps to that of the inorganic complex ion suggests the ionic nature of these soaps.

The infrared absorption spectra of these soaps and the parent complexes are shown in Figs. 2 and 3 and in Table II. Since carboxylate absorptions at 1400 and 1540 cm^{-1} are clearly found in them, it is evident that they are truly ionic. Absorptions of ammonia bending appeared as several bands around 1320 cm^{-1}, and as a broad band 1550~1600 cm^{-1}.

The specific magnetic susceptibility of cobalt

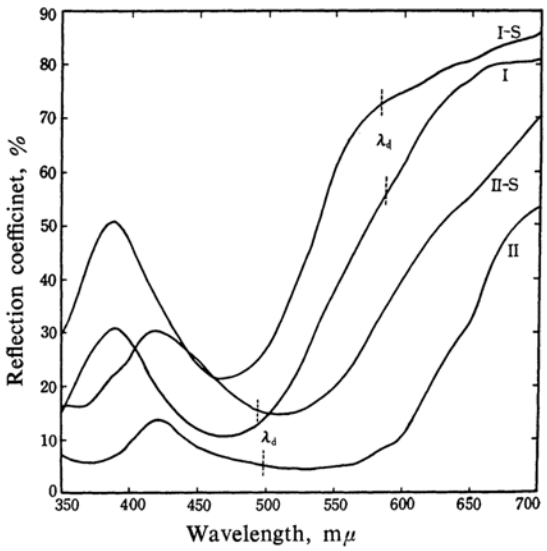

Fig. 1. Reflection spectra of cobalt complexes and cobalt complex soaps.

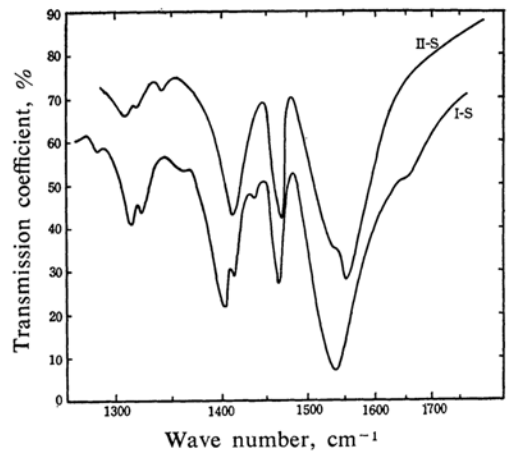

Fig. 2. Infrared absorption spectra of cobalt complex soaps.

* Present address: Aeronautical Research Institute, the University of Tokyo, Meguro-ku, Tokyo.

1) H. Kambe, This Bulletin, 34, 1786, 1790, 1794 (1961); 35, 78, 265, 269 (1962); H. Kambe and I. Mita, ibid., 34, 1797 (1961); H. Kambe, T. Ozawa, M. Onoue and S. Igarashi, ibid., 35, 81 (1962).

TABLE I. TRICHROMATICITY CONSTANTS OF COBALT COMPLEXES AND THEIR STEARATES

System	Tristimulus values			Trichromatic coeff.			Dominant wavelength, purity and brightness		
	X	Y	Z	x	y	z	λ_d	p_c	Y
I, $[Co(NH_3)_6]Cl_3$	48.19	41.46	15.82	0.457	0.393	0.150	587	60	41.46
I-S, $[Co(NH_3)_6]St_3$	61.45	58.01	30.60	0.410	0.386	0.204	583	45	58.01
II, $[Co(NH_3)_5Cl]Cl_2$	12.41	77.69	10.34	0.408	0.253	0.339	499c	44	77.69
II-S, $[Co(NH_3)_5Cl]St_2$	34.04	26.28	27.75	0.387	0.298	0.315	494c	22	26.28

TABLE II. INFRARED ABSORPTION SPECTRA OF COBALT COMPLEXES AND THEIR STEARATES*

	Sym. bend. NH_3		Bend. CH_2			Degener. bend. NH_3		
I, $[Co(NH_3)_6]Cl_3$	s 1326		sh 1356			d,m 1600		
II, $[Co(NH_3)_5Cl]Cl_2$	s 1310		w 1368	sh 1420		d,m 1550		
			sym. str. COO^-			asym. str. COO^-		
I-S, $[Co(NH_3)_6]St_3$	m 1312	sh 1321	s 1398	sh 1443	m 1459	s 1466	s 1542	
II-S, $[Co(NH_3)_5Cl]St_2$	w 1310	sh 1318	w 1340	m 1412		m 1468	sh 1542	s 1557

* s: strong; m: medium; w: weak; sh: shoulder; d: diffuse

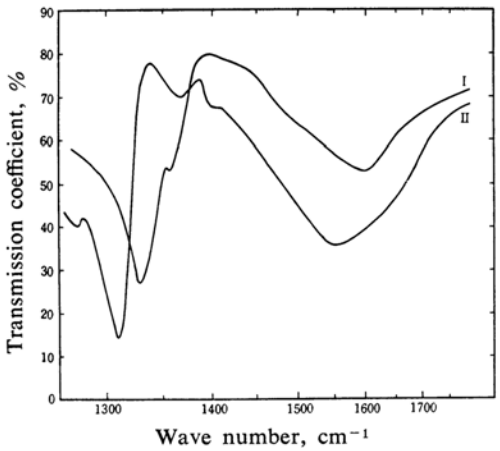

Fig. 3. Infrared absorption spectra of cobalt complexes.

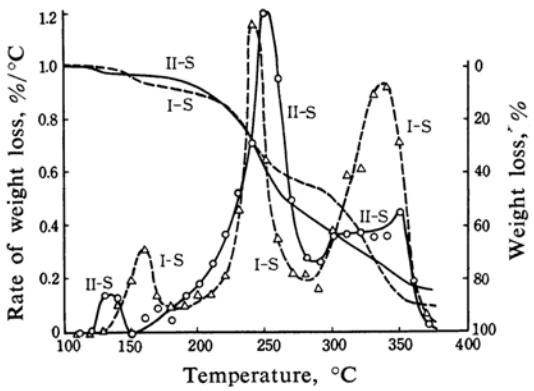

Fig. 4. Thermogravimetric curves of cobalt complex soaps.

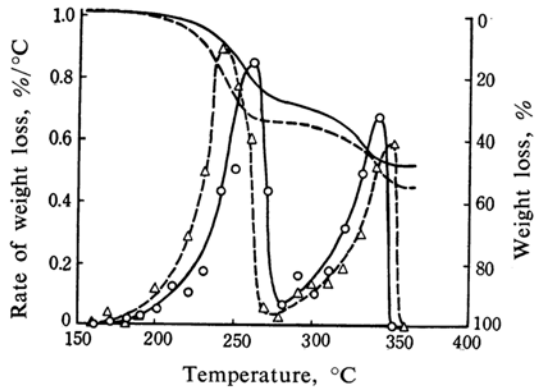

Fig. 5. Thermogravimetric curves of cobalt complexes.

complex soap I-S was measured as -0.58×10^{-6} c. g. s. Its molar susceptibility was calculated as -587.54×10^{-6} c. g. s. As the diamagnetic susceptibility of stearate ion is -209×10^{-6}, and that of cobalt(III) complex ion is -38×10^{-6}, the calculated value of the diamagnetic susceptibility of cobalt complex soap is -665×10^{-6} c. g. s., which is consistent with the observed value. In consequence, cobalt ion in cobalt complex soap is in the octahedral six-covalent electronic configuration, $(3d)^2(4s)(4p)^3$.

The decomposition curves of the cobalt complex soaps are shown in Fig. 4, and that of their parent inorganic complexes in Fig. 5. Inorganic complexes decompose at two stages. The first decomposition begins at 150°C and, through a maximum rate at 230°C for I and at

260°C for II, ends at 280°C. The second decomposition begins at 280°C and ends at 350~360°C, through a maximum rate at 350°C for I and 340°C for II. These peaks correspond to the liberation of ammonia at the first peak and of chlorine at the second peak. The residue is cobalt chloride.

The decomposition curves of cobalt complex soaps show three peaks. At the first peak ammonia is liberated, which is certified by an insertion of litmus paper in it. At the second peak, the white crystal deposits on the inner wall of the glass tube surrounding the reaction chamber, as was also observed in the decomposition of simple cobalt soaps (Part VI). At this stage, about one molecule of stearic acid is liberated as stearone from each soap. The last peak differs greatly between the two soaps. The remainder of stearic acid in the soap must be liberated, but stearone is not observed in this stage. The intermediate reaction products were not confirmed. The residue contains cobalt oxide in both cases.

Summary

Soaps of cobalt complex ions and fatty acid have been prepared and investigated. Reflection spectra and infrared spectra show that these soaps are ionic in nature, as is simple cobalt soap. The magnetic susceptibility of complex soap shows that cobalt ion is in the electronic configuration of octahedral six-covalent cobalt-(III) ion. Thermogravimetric analysis of these soaps shows that they decompose at three stages, but the precise mechanism of these reactions has not yet been determined.

The author expresses his gratitude to Professor Bunnosuke Yamaguchi for his advice throughout these studies, and to Messrs. Itaru Mita and Shoichi Igarashi for their help in the experiments.

Institute for Science and Technology
and Aeronautical Research Institute
The University of Tokyo
Meguro-ku, Tokyo