Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. IV. Ionic Nature of Cobalt Soaps, Revealed in Infrared Absorption Spectra and Magnetic Susceptibilities

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(Received March 11, 1961)

In the previous papers of these studies[1-3], three forms of cobalt soap with different colors—in other words, with different degrees of hydration—were found. As they are salts of fatty acid, they must be composed of cobalt and fatty acid ions.

In the present paper, their infrared absorption spectra and magnetic susceptibilities are measured. It is concluded that as the infrared absorption bands of carboxylate ion are found, these soaps are essentially ionic in nature. Magnetic moments of cobalt ion in these soaps, calculated from magnetic susceptibilities, support this conclusion.

Infrared spectra of cobalt salts of normal fatty acids, from formic to stearic acid, were observed by Duval, Lecomte, and Douvillé[4]. They confirmed that the carboxylic groups in these salts are essentially ionic in nature.

Herron and Pink[5] measured the magnetic susceptibilities of cobalt stearate and laurate, and of cobalt laurate dihydrate. The magnetic moments of cobalt ions in these soaps were given as $\mu_{\mathrm{eff}}=5.00$, 5.06 and 5.07 BM respectively. Moreau and Vatteroni[6] measured the magnetic susceptibilities of the cobalt salts of fatty acids with carbon numbers between 1

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[1] H. Kambe, This Bulletin, **34**, 1786 (1961).

[2] H. Kambe, ibid., **34**, 1790 (1961).

[3] H. Kambe, ibid., **34**, 1794 (1961).

[4] C. Duval, J. Lecompte and F. Douvillé, *Ann. phys.*, [11], **17**, 5 (1942).

[5] R. C. Herron and R. C. Pink, *J. Chem. Soc.*, **1956**, 3948.

[6] C. Moreau and M. Vatteroni, *Compt. rend.*, **237**, 1090 (1953).

and 18. They have found that the susceptibilities of cobalt salts of higher fatty acids are somewhat larger than that of inorganic cobalt sulfate.

The experimental results obtained in the present paper will be discussed in comparison with these investigations.

Experimental

Materials.—Cobalt stearate, palmitate, and myristate, of each typical color, obtained in the previous paper1) were used as samples. Stearic acid, sodium stearate, and cobalt hydroxide, which had been purified as usual, were used references to the infrared investigations.

Infrared Absorption Spectra.—Infrared absorption spectra were measured chiefly with a Perkin Elmer Model 112 single beam spectrophotometer, using a sodium chloride or calcium fluoride prism. Some samples were measured also with a Perkin Elmer Model 12B double beam spectrophotometer at the Laboratories of Mitsubishi Kasei Co[*2].

As cobalt soaps are generally insoluble in common solvents, powdered samples were used in the form of potassium bromide disks, or mulls in Nujol or in hexachlorobutadiene (HCB).

The potassium bromide disk method was used mainly in the range of wave number below 1700 cm^{-1}. The sample soaps and potassium bromide were carefully dried and pulverized to pass through a sieve of 200~250 meshes per inch. A small percentage was mixed with potassium bromide powder and pressed at 10,000 kg./cm^2 to form a disk.

Above 2700 cm^{-1}, the Nujol mull or HCB mull method was used exclusively. Mulls were placed between rock salt plates. Nujol shows strong absorptions of C-H bond, which overlap C-H absorptions of the soap. Although HCB is so volatile that it is difficult to make mulls with it, it was chiefly used in the range of 2700~4000 cm^{-1}, for it shows no absorption above 1700 cm^{-1}.

Magnetic Constants.—The magnetic susceptibility χ_H of cobalt soap, mixed with zinc oxide, was measured by Gouy's method[*3]. χ_H was corrected for ferromagnetic imprities by plotting susceptibilities against reciprocal field strength. Extrapolation to infinite field strength gives χ_∞, which is substantially free from ferromagnetic effects.

As the specific susceptibility of zinc oxide, χ_{ZnO}, had been given as -0.26×10^{-6} c. g. s., the specific susceptibility of soap, χ, was determined by the following formula:

$$\chi_\infty=\frac{w}{100}\chi+\frac{100-w}{100}\chi_{ZnO} \tag{1}$$

in which w is the concentration of soap in per cent by weight. Molar susceptibility is calculated by a formula:

$$\chi_M=M\cdot\chi \tag{2}$$

in which M is the molecular weight of soap.

The diamagnetic component of susceptibility, $\sum\chi_{dia}$, was corrected by a formula

$$\chi_M=\chi_{para}+\sum\chi_{dia} \tag{3}$$

The diamagnetic susceptibilities of the constituents of which are shown in Table I.

The magnetic moments in Bohr magneton (BM) were calculated by a formula:

$$\mu_{eff}=2.839\sqrt{\chi_{para}\cdot T}\quad(\mathrm{BM}) \tag{4}$$

TABLE I. SPECIFIC DIAMAGNETIC SUSCEPTIBILITIES, $-\chi_{dia}\cdot10^6$ (c.g.s./g.)

Stearate ion	209*
Hydration water	13 7)
Cobalt(II) ion	12 8)

* This value was found in magnesium, zinc and cadmium stearates7).

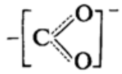
Results and Discussion

Infrared Absorption Spectra.—The wave numbers of the absorption maxima in the infrared spectra of cobalt soaps are assigned and tabulated in Tables II and III.

Absorptions by Hydrocarbon Chain. — Among species of the same color, the chain length of fatty acid did not significantly influence the spectrum. Band progression at 1200~1300 cm^{-1}, due to hydrocarbon chain, depends to some extent upon the length of the chain, but the absorption bands of cobalt soaps are weaker than that of stearic acid.

The absorption bands of C-H stretching vibrations, i. e. the out-of-phase vibration of CH_2 at 2865, the in-phase one at 2935, and the asymmetrical vibration of CH_3 at 2970 cm^{-1}, and the bands of symmetrical bending of CH_2 at 1465 cm^{-1} were always observed in all soaps, without distinction of color. The symmetrical bending vibration band of CH_3 at 1375 cm^{-1} was found in red soaps, but in other soaps it was not readily indentified.

Absorptions by Carboxylate Ion. — Absorption spectra in the range of 1250~1800 cm^{-1} are shown in Figs. 1—3.

It is well known that in free fatty acid carboxyl groups of two molecules are donded by hydrogen bonds to take a dimeric form. The absorption of a carboxyl group in this state reveals its C=O stretching vibration band near 1700 cm^{-1} (cf. Table III). In cobalt soaps, two absorption bands of carboxyl group were found at 1400 and 1550 cm^{-1}, instead of one band at 1700 cm^{-1}. They correspond to the symmetric and antisymmetric stretching vibrations of carboxylate ion,  , as

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[*2] With the latter instrument, measurements were executed by Mr. S. Morita.

[*3] Magnetic measurements were carried out by Dr. Y. Matsunaga at Department of Chemistry, Faculty of Science, The University of Tokyo.

7) M. Prasad, C. R. Kanekar, S. P. Walvekar and D. D. Khanolkar, *J. Chem. Phys.*, **18**, 936 (1950).

8) P. W. Selwood, *Chem. Revs.*, **38**, 41 (1946).

TABLE II. INFRARED ABSORPTION SPECTRA OF COBALT SOAPS MEASURED WITH A P. E. 112 SPECTROPHOTOMETER (cm^{-1})*

System	Progression bands					Sym. bend. CH_3	Sym. str. COO^-	Asym. bend. CH_3	Sym. bend. CH_2	Asym. str. COO^-	Out-of-phase str. CH_2	In-phase str. CH_2	Asym. str. CH_3	Str. OH	
(Pink soaps)															
Cobalt stearate	w 1270	w 1284	w 1303	w 1320	w 1336		s 1410	s 1441	s 1467	s 1559	s 2870	s 2940	m 2970	s 3300	
Cobalt palmitate	w 1260	w 1288	w 1297	w 1318	w 1334		s 1410	s 1441	s 1467	s 1559	s 2870	s 2940	m 2970	s 3290	
Cobalt myristate		w 1290		w 1316	w 1334		s 1410	s 1441	s 1467	s 1559	s 2870	s 2940	m 2970	s 3300	
(Blue soaps)															
Cobalt stearate		w 1287	1307	w 1322	w 1340		m 1396		m 1461	s 1525	s 2860	s 2935	m 2970		
Cobalt palmitate			w 1297	w 1322	w 1340		m 1396		m 1461	s 1523	s 2860	s 2935	m 2970		
Cobalt myristate			w 1296	w 1322	w 1341		m 1396		m 1461	s 1523	s 2860	s 2935	m 2970		
(Red soaps)															
Cobalt stearate		w 1285	w 1305	w 1322	w 1336	w 1374	s 1412		s 1470	s 1535	s 2865	s 2935	m 2970	s 3260	s 3400
Cobalt palmitate		w 1278	w 1296	w 1322	w 1340	w 1376	m 1412		s 1469	s 1534	s 2865	s 2935	m 2970	s 3260	s 3400
Cobalt myristate			w 1292	w 1318	w 1340	m 1374	s 1412		s 1468	s 1532	s 2865	s 2935	m 2970	s 3260	s 3400

TABLE III. INFRARED ABSORPTION SPECTRA OF COBALT SOAPS MEASURED WITH A P. E. 21B, BY KBr DISK METHOD (cm^{-1})*

System	Rocking CH_2		Out-of-plane deform. OH	Str. C-C	Progression bands	Sym. str. COO^-		Asym. bend. CH_3	Sym. bend. CH_2	Asym. str. COO^-	Str. C=O	Str. OH	Out-of-phase str. CH_2	In-phase str. CH_2	Asym. str. CH_3
Blue cobalt stearate	w 720			w 1110	v. w several	m 1400			m 1468	m 1532			s 2850	s 2920	sh 2970
Red cobalt stearate	w 720			w 1110	v. w several	m 1415			m 1470	s 1532			s 2850	s 2920	sh 2970
Sodium stearate	w 720			v. w 1110	v. w several	m 1424		m 1445	m 1475	s 1560			s 2850	s 2920	sh 2960
Stearic acid	m 720	m 730	m 940	w 1110	w 1190~1300	m 1412	m 1432		m 1468		s 1700	d. m 2650	s 2850	s 2920	sh 2960

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

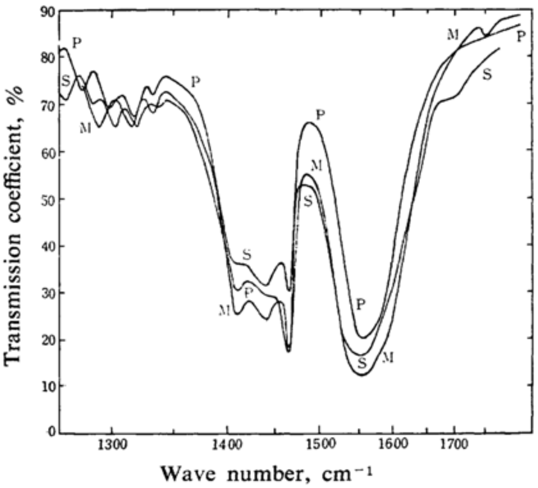


Fig. 1. Infrared absorption spectra of pink cobalt soaps.

S: Cobalt stearate P: Cobalt palmitate
M: Cobalt myristate

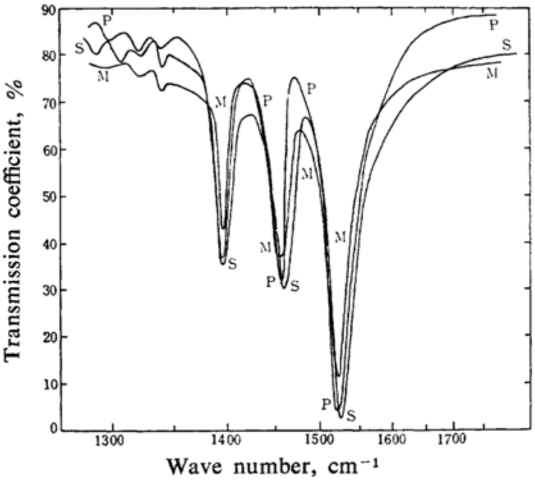


Fig. 2. Infrared absorption spectra of blue cobalt soaps.

S: Cobalt stearate P: Cobalt palmitate
M: Cobalt myristate

pointed out by Duval, Lecompte and Douvillé[4]. Their conclusion was based on the deformation vibration modes of carboxylate ions, appearing at lower frequency range than ours. Their results were stated to be uncertain at a higher frequency range owing to the insufficient resolving power of their instrument.

From this result it has been concluded definitely that all cobalt soaps obtained in our experiments are ionic in nature. As a reference, spectra of free stearic acid and sodium stearate are shown in Table III. Stearic acid distinctly shows a stretching vibration of C=O at 1700

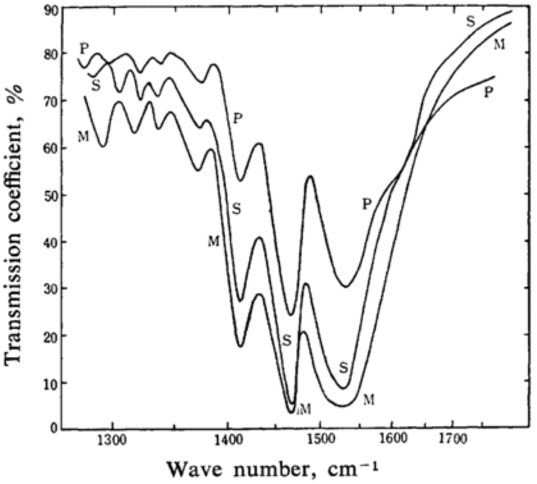
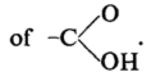


Fig. 3. Infrared absorption spectra of red cobalt soaps.

S: Cobalt stearate P: Cobalt palmitate
M: Cobalt myristate

cm⁻¹, while no band was found at 1550 cm⁻¹ corresponding to the antisymmetric vibration of carboxylate ion. In place of the symmetric stretching band of carboxylate ion at 1400 cm⁻¹, there appeared the C–O stretching band and O–H in-plane deformation band of  $-\mathrm{C}\begin{matrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{matrix}$.

Naturally, the OH stretching band at 2650 cm⁻¹ and the OH out-of-plane deformation band at 940 cm⁻¹ appeared in the spectrum of stearic acid.

Sodium stearate shows carboxylate bands at 1424 and 1560 cm⁻¹ and an absorption by the asymmetrical bending of CH_3 at 1445 cm⁻¹, which appears in pink soaps, exclusively. This may indicate the similarity between sodium soap and pink cobalt stearate.

Absorptions by Hydroxyl Bond. — In spectra of cobalt soaps with different colors of the same fatty acid, several differences were found.

In red and pink soaps, absorptions by stretching vibration of OH bonds appeared in the 3200～3400 cm⁻¹ region, but in blue soaps they were completely lacking. This is in accordance with the results of analyses of water content[2]. In pink soaps, a broad peak reveals itself at 3300 cm⁻¹, but in red soap, two peaks appear at 3260 and 3400 cm⁻¹.

The hydroxyl bond of cobalt hydroxide shows a very sharp band of free OH vibration at 3640 cm⁻¹, which does not exist in the spectrum of every soap. Liquid water shows a peak of hydrogen-bonded OH at 3410 cm⁻¹. In comparison with these data, water molecules in cobalt soaps were attached to cobalt ion with stronger bonds than hydrogen-bonds in

TABLE IV. MAGNETIC CONSTANTS OF COBALT SOAPS (T=297°K)

	$\chi_H\cdot10^6$		$\chi_\infty\cdot10^6$	w	$\chi\cdot10^6$	$\chi_M\cdot10^6$	$\sum\chi_{dia}10^6$	$\chi_{para}\cdot10^6$	μ
	H=22500	16400	(calcd.)	wt. %					BM
	$1/H\cdot10^4$=0.444	00610	0						
Red cobalt						(M=661.89)			
stearate	3.16	3.37	2.59_8						
dihydrate	3.07	3.27	2.53_5						
			Av. 2.57	19.8	14.0_3	9286.3	−456	8830.3	4.59_7
Blue cobalt						(M=625.86)			
stearate	2.48	3.57	2.23_9						
anhydrate	2.51	2.61	2.24_2	18.8	13.0_3	8155.0	−430	7725.0	4.30_0
			Av. 2.24						

TABLE V. ELECTRONIC CONFIGURATIONS OF COBALT(II) COMPLEXES[9,10]

Type	Coordination number	Geometry of complex	Electronic configurations 3d	4s	4p	4d	5s	Hybrid orbitals	Observed magnetic moment μ_{eff}, BM
Free Co^{2+} ion			[↓↑][↓↑][↓][↓][↓]	[ ]	[ ][ ][ ]	[ ][ ]	[ ]		
Spin-free or ionic covalent	6	octahedral	[↓↑][↓↑][↓][↓][↓]	[××]	[××][××][××]	[××][××]	[ ]	(4s)(4p)^3(4d)^2	4.9∼5.6
	4	tetrahedral	[↓↑][↓↑][↓][↓][↓]	[××]	[××][××][××]	[ ][ ]	[ ]	(4s)(4p)^3	4.3∼4.8
	4	square, planar	[↓↑][↓↑][↓][↓][↓]	[××]	[××][××][ ]	[××][ ]	[ ]	(4s)(4p)^2(4d)	4.8∼5.4
Spin-paired covalent	4	square, planar	[↓↑][↓↑][↓↑][↓][××]	[××]	[××][××][ ]	[ ][ ]	[ ]	(3d)(4s)(4p)^2	2.1∼2.9
	6	presumably tetragonal (a)	[↓↑][↓↑][↓↑][↓][××]	[××]	[××][××][××]	[××][ ]	[ ]	(3d)(4s)(4p)^3(4d)	1.7∼2.0
		(b)*	[↓↑][↓↑][↓↑][××][××]	[××]	[××][××][××]	[ ][ ]	[↓]	(3d)^2(4s)(4p)^3	

[××] : Bonding orbitals.
* Figgis and Nyholm[9] proposed originally this configuration, but considered later that this improbable.

free water. Therefore, it was concluded that water in cobalt soaps exists as hydration water.

Magnetic Susceptibilities. — Observed values of magnetic susceptibilities and magnetic moments, calculated as stated above, of red and blue cobalt stearates are shown in Table IV.

Figgis and Nyholm[9] have shown that, according to magnetic moment, cobalt(II) compounds may be classified into two types, that is, the spin-free or ionic covalent type and the spin-paired covalent type, as shown in Table V. The number of unpaired electrons, n, in these configurations is three and one. Therefore, the spin only value of magnetic moment, $\mu_{eff}=\sqrt{n(n+2)}$, is 3.88 and 1.73 BM, respectively. The observed values of many complexes of each type were 4.2∼5.6 BM in the spin-free type, and 1.7∼2.9 BM in the spin-paired type, as shown in Table V.

On the basis of these facts it has been concluded that the cobalt soaps used in the present paper were spin-free or ionic covalent complexes. This conclusion is completely consistent with the results of infrared absorption measurements.

Observed values of magnetic moments of cobalt(II) complexes are generally larger than spin only values, for the contribution of the orbital motion of electrons was not completely quenched in them owing to the presence of ligand fields and spin-orbit couping. Among ionic covalent complexes, the orbital contribution is smaller in tetrahedral sp^3 orbitals than in octahedral sp^3d^2 orbitals. This is based on the difference of multiplicities of ground states in these configurations[10].

Although our values are somewhat smaller than that of Figgis and Nyholm, blue and red cobalt soaps must correspond to the (4s)(4p)^3 tetrahedral four-covalent complex and the (4s)(4p)^3(4d)^2 octahedral six-covalent complex respectively. Holm and Cotton[10] have proposed the (4s)(4p)^2(4d) square planar, ionic covalent type for some cobalt(II) complexes, but this configuration may be excluded from our cases by considerations of color.

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9) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1954**, 12; **1959**, 331, 338.

10) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959); 32, 1168 (1960); *J. Am. Chem. Soc.*, **82**, 2979, 2983 (1960).

The magnetic moments of rose-pink cobalt laurate dihydrate and purple anhydrate of cobalt stearate and laurate obtained by Herron and Pink⁵⁾ were larger than our values, as has been shown before. In contrast with our results, they found no difference in magnetic moments between anhydrate and dihydrate of cobalt laurate. As their purple anhydrate was prepared by boiling rose-pink dihydrate with solvent, it might be a glassy form recovered from a molten state. In our experiments, which will be discussed in a later part of these studies, a once-melted soap showed a somewhat larger magnetic moment than a true blue form. The orbital contribution is so much affected by a crystal field¹⁰⁾ that the melted form must have a different contribution of orbital motion to the magnetic moment.

Moreau and Vatteroni⁶⁾ compared the magnetic susceptibilities of cobalt soaps with that of cobalt sulfate and found that the values of cobalt soaps were somewhat larger than inorganic salt. They concluded that these soaps were regarded as structure complexes. This is also consistent with our results.

Structure Formulas of Cobalt Soaps.—From these results, it may be concluded that red dihydrate and blue anhydrate of cobalt stearate have a geometry of octahedral and tetrahedral coordination complex respectively. The structure formulas of these soaps may be described as shown in Fig. 4, following Herron and Pink⁵⁾. Such a formula was proposed for cupric salts of lower fatty acids by French and Lowry¹¹⁾ and opposed by Sidgwick¹²⁾. Sidgwick's main reason for rejecting this formula was that the strain in the chelate ring of four members makes them exceedingly unstable. The alternative formula, in which the carboxyl group occupies two coordination positions attaching themselves to two different cobalt ions, so as to form a ring of more than four members, must be proposed. This was done in cupric soaps⁵⁾, but not yet for cobalt soaps.

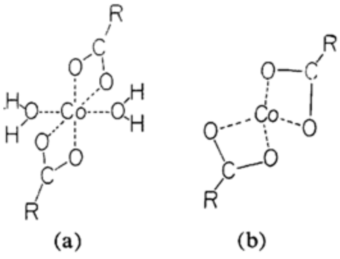

Fig. 4. Proposed structure formulas of cobalt soaps.

(a) Red dihydrate (b) Blue anhydrate

Summary

The infrared absorption spectra and the magnetic susceptibilities of red dihydrate and blue anhydrate of cobalt stearate were measured. The infrared spectra showed the existence of carboxylate ion in these soaps, and magnetic measurements confirmed that they are ionic in nature.

The magnetic moments of red and blue cobalt stearates showed that they are spin-free or ionic covalent complexes. The geometry of red soap is six-covalent octahedral, and that of blue is four-covalent tetrahedral. Structure formulas were proposed for them in correspondence with these geometries, but they may be improbable because of the existence of unstable rings of four members. Alternative formulas, in which a carboxyl group joins two cobalt ions, might be considered but have not yet been given.

The authors express their gratitude to Professor Bunnosuke Yamaguchi for his advice throughout this work, and to Dr. Yoshio Matsunaga and Mr. Shiro Morita for their accomplishments in magnetic and some infrared absorption measurements.

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11) H. S. French and T. M. Lowry, *Proc. Roy. Soc.*, **106A**, 489 (1924).

12) N. V. Sidgwick, "The Electronic Theory of Valency", Oxford Univ. Press, Oxford (1927), p. 252.