Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. V. Appearances, Densities, and X-Ray Analysis of Crystal Structures of Cobalt Soaps

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In the previous papers of this study[1], three species of cobalt soap with different colors were investigated. They differ so much from each other to the eye and also, more especially, to the touch, that their crystallinities must be distinguishable. In the present parer, microphotographs of their appearances are shown, and apparent densities in air and in acetone, and true densities are measured. Moreover, X-ray analysis of these soaps is carried out.

X-Ray analysis of cobalt stearate and palmitate was executed by Vold and Hattiangdi[2]. However, as they had dried their soaps in an oven, their samples perhaps took a melted form which showed only an amorphous halo in the X-ray pattern. Our soaps, prepared in cold, are truly crystalline. But unfortunately, no adequate solvent was found for them, so single crystals of cobalt soaps have not yet been obtained. Complete X-ray analysis of their crystal structures must be reserved for the future.

Experimental

Materials. — The same cobalt stearates in three typical colors were used, as in the previous papers[1].

Microphotography.—Soap powder, passed through a sieve of 100 meshes per inch, was scattered on a glass plate in the field of a microscope. Microphotographs of 300 magnifications were taken with transmitted light.

Density Measurement. — The apparent packing densities of cobalt soap powders in air were measured in a graduated glass tube. Apparent volume was measured directly after the settling of the powder and after a gentle tapping of about 300 times. Finally the tube was inverted and the packing of the powder was observed. The sedimentation volume of soap powder in acetone was measured with the lapse of time in the same tube. Apparent densities in acetone were calculated. True densities of powder were measured with a substitution method in acetone. Acetone was chosen because the color of soaps did not change at all in it.

Powder X-Ray Analysis. — Debye-Scherrer's method was applied to soap powders*2. Powder was pushed into a glass capillary and extruded by a wire. A cylinder formed by soap with a length of 1~2 mm. and a diameter of about 0.5 mm. was barely attached to a sample holder at the center of a cylindrical camera. The camera radius, R, was 57.44 mm. The radiation used was CuKα with a nickel filter.

X-Ray diffraction patterns were analyzed with a microphotometer, and the diffraction angle θ was calculated by the formula:

$$L=2\theta\cdot R \qquad (1)$$

in which L is the distance of a diffraction line from the center of the film. Lattice spacing d was calculated by Bragg's formula:

$$2d\sin\theta=n\lambda \qquad (2)$$

in which n is an order of diffraction, λ is a wavelength of incident X-rays; in this case $\lambda(\mathrm{CuK}\alpha)=1.539$ Å.

Results and Discussion

Appearances.—Blue cobalt stearate was clearly crystalline and easily removable from filter paper in a dry state, but it was hard to pulverize it. Pink soap was rather plastic to the touch, like fatty acid, and adhered to filter paper after drying. Often it was charged electrically when it was removed from filter paper. When pulverized, it became a fluffy powder. Red soap was most easily pulverized, did not stick together, and freely flowed.

Crystal forms of powdered red and blue cobalt stearates are shown in microphotographs in Fig. 1. In blue soap powder some prismatic crystals are found, but in red soap only plate-like crystals exist in the field. Crystal forms of red soap are very similar to that of stearic acid.

Densities.—The apparent densities of cobalt stearates with different colors were distinguishable from each other. Packing densities in air are shown in Table I. In this state blue soap is much denser than red soap, and pink soap is between them. This is because of the difference in their crystalline forms.

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1) H. Kambe, This Bulletin, **34**, 1786, 1790, 1794 (1961); H. Kambe and I. Mita, ibid., **34**, 1797 (1961).

2) R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).

*2 X-Ray measurements were carried out at Physics Department, Inst. Sci. Techn., following the advice of Mr. T. Sakurai.

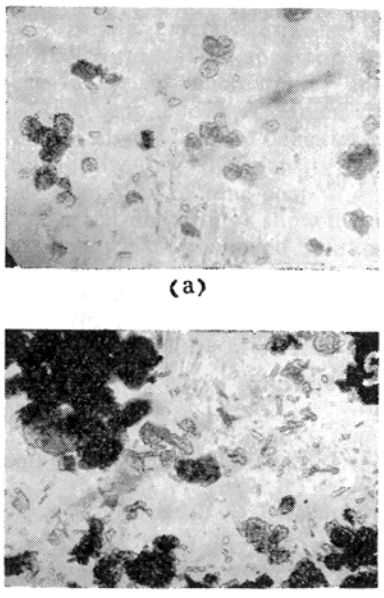

Fig. 1. Appearances of cobalt stearate crystals.
(a) Red dihydrate; (b) Blue anhydrate

TABLE I. APPARENT DENSITIES OF COBALT STEARATE POWDERS IN AIR (g./ml.)

Color of cobalt soap	After settling	After tapping 300 times	After inversion
Blue	0.195	0.333	0.221
Red	0.150	0.246	0.149
Pink	0.173	0.278	0.179

The apparent densities in acetone are shown in Table II. Sedimentation volumes of cobalt soaps in acetone gradually become smaller. In this case, the density of the blue form is also the highest, as in air. But red and pink soaps reverse their densities in acetone and air. Red form was apparently much denser in acetone.

True densities, measured with a substitution method in acetone at 25°C, are tabulated in Table III. It is found that the density of red soap is slightly larger than that of blue soap, in contrast with the apparent densities. This may be due to the difference in their crystalline structure.

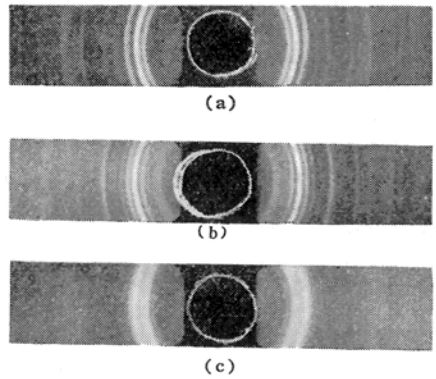

Fig. 2. X-Ray diffraction patterns of cobalt soaps.
(a) Stearic acid; (b) Red cobalt stearate dihydrate; (c) Blue cobalt stearate anhydrate

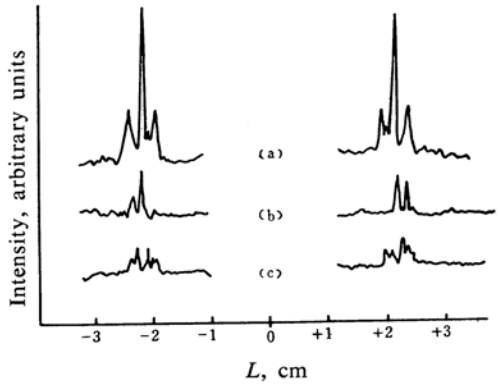

Fig. 3. Microphotometric curves of X-ray patterns.
(a) Stearic acid; (b) Red cobalt stearate dihydrate; (c) Blue cobalt stearate anhydrate

X-Ray Analysis. — The X-ray diffraction patterns of blue and red cobalt soaps and stearic acid are shown in Fig. 2, and their microphotometric curves are shown in Fig. 3. The main diffraction lines are tabulated in Table IV.

Red soap shows a pattern which is very

TABLE II. APPARENT DENSITIES OF COBALT STEARATE POWDERS IN ACETONE (g./ml.)

Color of cobalt soap	Weight, g.		Directly	After				
	Soap	Acetone		20 min.	2 hr.	4.5 hr.	2 days	6 days
Blue	1.015	6.871	0.139	0.156	0.171	0.181	0.209	0.228
Red	0.468	7.253	0.096	0.170	0.184	0.195	0.204	0.213
Pink	0.934	7.080	0.139	0.144	0.144	0.148	0.158	0.164

TABLE III. TRUE DENSITIES OF COBALT STEARATES (25°C)

Red soap:	1.251, 1.321, 1.229, 1.232, 1.281	Av. 1.263
Blue soap:	1.185, 1.222, 1.207, 1.304, 1.195, 1.199, 1.187, 1.205	Av. 1.213

TABLE IV. X-RAY DIFFRACTION LINES OF TYPICAL COBALT STEARATES AND STEARIC ACID*1

Stearic acid*2			Red soap			Blue soap	
	sin θ	d/n		sin θ	d/n	sin θ	d/n
w	0.092	8.37*3					
m	0.169	4.56	(4.12)*4	w 0.129	5.97*3		
w	0.178	4.32		w 0.172	4.47	(4.04)*4	
vs	0.187	4.12		s 0.190	4.05	s 0.171	4.50
s	0.208	3.70		m 0.205	3.75	s 0.178	4.32
w	0.236	3.26		w 0.217	3.54	s 0.182	4.23
w	0.273	2.82		w 0.241	3.19	vs 0.198	3.89
w	0.311	2.47		w 0.260	2.96	s 0.205	3.75
				w 0.274	2.81	s 0.208	3.70

*1 s: strong; vs: very strong; m: medium; w: weak.
*2 Without nickel filter.
*3 Higher order of long spacing.
*4 The values in parentheses were calculated as CuKβ (λ=1.389 Å) diffraction. These lines were weakened by a nickel filter.

similar to that of stearic acid. It is characteristic of this pattern that a strong line exists between two medium lines, the inner one of which was weakened by the attachment of a nickel filter. Blue soap shows a quite different pattern, in which two groups of strong lines are characteristic.

Fatty acid and its derivatives usually exhibit crystals of a monoclinic system. Their crystal structure is composed alternately of ionic layers and hydrocarbon layers, stacked on one another. The resemblance of the X-ray pattern of red soap to that of fatty acid means that this species also has such a layer structure. Pink soap also shows such a layer structure pattern, and so it is evident that there is a similarity of structure between these soaps. The water molecules contained in red dihydrate must be attached directly to cobalt ion. The coordination number of six, which has been found by magnetic measurement on red soap[1], must be fulfilled by joining two cobalt ions together by carboxylate ions. Such a structure has been proposed by Stanley[3] for calcium stearate monohydrate.

It is certain, because of the difference in coordination numbers and X-ray patterns, that blue soap has a different structure from pink and red soaps, but X-ray analysis of crystals has not yet been executed on single crystals. The confirmation of the exact crystal structure must therefore be postponed.

Purple soaps, which were obtained from red or pink soaps immersed in absolute ethanol, showed a diffraction pattern from the blue type, but violet soap, which was half turning red from blue, showed a red-type pattern. Melted soap always showed a diffuse halo, as shown by Vold and Hattiangdi[2].

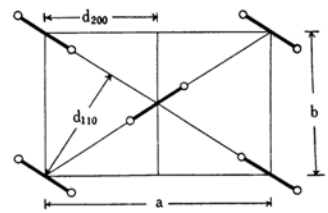

Fig. 4. Schematic diagram of a besal plane of unit cell in red cobalt stearate dihydrate. Dumbbells show orientations of paraffinic chains in crystal lattice.

The diffraction pattern of red soap was analyzed in the same way as Müller[4] had done on normal paraffins. A basal plane of paraffinic lattice may be described as Fig. 4. A lattice spacing obtained from the most intense diffraction line in an X-ray pattern of this type was identified as d_{110}; the outer medium line was d_{200}, and the inner medium CuKβ-diffraction of d_{110}, which was weakened line was by a nickel filter.

From the observed values of diffraction angles in red soap, d_{110}=4.05 Å and d_{200}=3.75 Å. From these, the lattice constants of red cobalt stearate were calculated as $a=2d_{200}$=7.50 Å, and b=4.81 Å. In the same way, stearic acid shows d_{110}=4.12 and d_{200}=3.70 Å. Therefore, in stearic acid, a=7.40 and b=4.96 Å. The lattice of red soap is broadened a little along the b axis and shortened along the a axis compared with acid.

Summary

Crystallinities of cobalt stearates with different colors have been compared. Blue soap

3) E. Stanley, *Nature*, 175, 165 (1955).

4) A. Müller, *Proc. Roy. Soc.*, A138, 514 (1932).

shows a prismatic crystal form, but red soap a plate-like form. The apparent density of blue soap in air is much denser than other soaps. Red soap shows a larger density in acetone than in air. True densities measured in acetone show that the density of red soap is higher than that of blue soap.

X-Ray diffraction patterns show the difference between red or pink soap and blue soap. Red soap has a lamellar structure like that of fatty acid, while blue soap shows a quite different structure. Exact X-ray analysis was not executed, however, because single crystals of cobalt soaps have not yet been obtained.

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