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On the Preparations of Metal Complexes. V. The Preparations of Cholatoamminecomplexes of Cobalt(III) and Chromium(III)

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The mono-, di- and tricholatocobalt(III) and chromium(III) complexes and cobalt complex cholates, including the following new compounds, have been prepared: [Co chol $(NH_3)_5$] X_2 (X =chol, Cl), [M $chol_2$ en_2]Cl (M=Co, Cr), [Co $chol_3$ $(NH_3)_3$] and [Co en_3]$chol_3$. The absorption spectra of these complexes in the visible, ultraviolet, and infrared regions have been measured and compared with those of the corresponding acetato- or acido-complexes.

A number of Werner-type complexes of cobalt(III) and chromium(III) which contain alkyl carboxylic acids are known at present. Two series of complexes, [M $(RCOO)_2$ en_2]$^+$ (M=Co(III) and Cr(III), R=CH_3 to $C_{17}H_{35}$) have been prepared by Linhard and Stirn[1] and by Nakahara.[2] The diacido-type [Co $(RCOO)_2$ $(NH_3)_4$]$^+$,[3] the monoacido-type [Co RCOO $(NH_3)_5$]$^{2+}$,[4] and the triacido-type [Cr $(CH_3COO)_3$ $(NH_3)_3$][5] have also been prepared. One of the present authors (M.N.) has prepared the diacido-type complexes, [M$(RCOO)_2$ en_2]$^+$ (M=Co(III), Cr(III)), containing fatty acids of various chain lengths (R=C_9H_{19} to $C_{17}H_{35}$) and has studied the *cis-trans* isomerisations.[2] It was found, in this investigation, that, in the case of the fatty acids, C>10, even though the *trans*-form complexes were used as the starting materials, the *cis*-form products were always obtained. This phenomenon has been explained in terms of the attraction between the long chains of the saturated fatty acids.

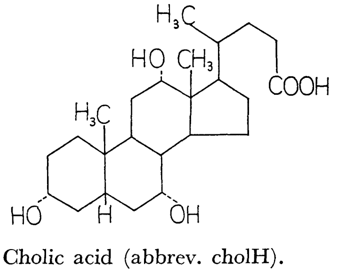

Fig. 1. Cholic acid (abbrev. cholH).

In the present work, cholic acid ($C_{24}H_{40}O_5$, cholH) (Fig. 1) is used as the carboxylic acid. This acid resembles the long-chain fatty acids mentioned above because the steroid skelton may be considered to be a condensed paraffin. However, it is rather different from the fatty acids in that the condensed part of the molecule is fairly bulky. Thus, it seemed that it would be interesting to compare the properties of cholatocomplexes with those of the fatty-acid complexes. For this purpose, three types of cholato complexes, [M chol $(NH_3)_5$]$^{2+}$, [M $chol_2$-en_2]$^+$, and [M $chol_3$ $(NH_3)_3$] (M=Co(III), Cr(III)) are prepared and their properties are investigated.

Experimental

Preparations. *1) Cholic Acid,* $C_{24}H_{40}O_5$. Reagent-grade cholic acid was dissolved in ethanol, and then, after active carbon had been added to the solution, it was recrystallized several times.

2) Sodium Cholate, $NaC_{24}H_{39}O_5$. Purified cholic acid was dissolved in water containing an equivalent amount of sodium hydroxide, and then the solution was evaporated to dryness on a water bath.

3) Silver Cholate, $AgC_{24}H_{39}O_5$. The sodium cholate was dissolved in water at about 50°C, and an aqueous solution of silver nitrate was added to this solution. The precipitate of the silver cholate was filtered, washed several times with water, acetone, and ether successively, and air-dried.

4) Tris(ethylenediamine)cobalt(III) Chloride, [Co en_3]-Cl_3,[6] *Chloropentaamminecobalt(III) Perchlorate,* [Co Cl $(NH_3)_5$] $(ClO_4)_2$,[7] *trans-Dichlorobis(ethylenediamine)cobalt(III) Chloride, trans*-[Co Cl_2 en_2]Cl,[6] *cis-Dichlorobis(ethylenediamine)cobalt(III) Chloride, cis*-[Co Cl_2 en_2]Cl,[7] *Trichlorotriamminecobalt(III),* [Co Cl_3 $(NH_3)_3$],[8] *trans-Dichlorobis(ethylenediamine)chromium(III) Chloride, trans*-[Cr

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[1] M. Linhard and G. Stirn, *Z. Anorg. Allg. Chem.*, **268**, 105 (1952).

[2] M. Nakahara, This Bulletin, **35**, 901 (1962).

[3] M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **260**, 65 (1949).

[4] M. Linhard and M. Weigel, *ibid.*, **264**, 321 (1951).

[5] M. Nakahara, This Bulletin, **35**, 782 (1962).

[6] "Inorganic Syntheses," Vol. 2, (1946), p. 221.

[7] *Ibid.*, Vol. 2, (1946), p. 223.

[8] M. Mori, M. Shibata, K. Hirota, K. Masuno and Y. Suzuki, *Nippon Kagaku Zasshi*, **79**, 1251 (1958).

Cl$_2$ en$_2$]Cl,9) *cis-Dichlorobis(ethylenediamine)chromium(III) Chloride*, *cis*-[Cr Cl$_2$ en$_2$]Cl.10) These complexes were synthesized according to the method for each.

5) Tris(ethylenediamine)cobalt(III) Cholate, [Co en$_3$]chol$_3$. Into a small amount of water we dissolved 0.4 g of [Co en$_3$]Cl$_3$, and then the solution was treated with freshly-precipitated silver oxide. The precipitate thus produced was filtered off, and 40 m*l* of methanol were added. One and a half grams of cholic acid in 40 m*l* of methanol were added to the solution, and the mixture was stirred. Then, after a large amount of ether had gradually been poured into the mixed solution, the solution was stirred vigorously with a glass rod until a yellow product was precipitated; this product was filtered, dissolved into methanol again, reprecipitated with ether, filtered, washed with ether, and then air-dried. Yield, 0.8 g (44%).

Found: Co, 4.21; C,[*1]; H, 9.66; N, 5.50%. Calcd: Co, 4.34; C,[*1]; H, 9.72; N, 5.75%.

Yellow powder, soluble in methanol, and insoluble in ether.

6) Chloropentaamminecobalt(III) Cholate, [Co Cl(NH$_3$)$_5$]chol$_2$. One and a half grams of [Co Cl (NH$_3$)$_5$](ClO$_4$)$_2$, 2 g of sodium cholate, and 2 g of cholic acid were suspended in methanol, after which the solution was gently heated on a water bath using a reflux condenser. After an hour, the unreacted materials were filtered off from the red solution. A large amount of acetone was added to the filtrate, and the red product which was thus immediately precipitated was filtered, washed with acetone, and air-dried. It was dissolved in methanol again and reprecipitated with acetone for purification. Yield, 2.4 g (45%).

Found: Co, 5.85; C,[*1]; H, 9.65; NH$_3$, 8.30%.

Calcd: Co, 5.92; C,[*1]; H, 9.42; NH$_3$, 8.56%.

Red powder, soluble in methanol, slightly soluble in ethanol, and insoluble in water, acetone, and ether.

7) Cholatopentaamminecobalt(III) Cholate, [Co chol(NH$_3$)$_5$]chol$_2$. In methanol we suspended 2.4 g of [CoCl (NH$_3$)$_5$]chol$_2$, 1 g of sodium cholate, and 1 g of cholic acid, after which, the solution was heated on a water bath with a reflux condenser. The fine purple-red crystals ([Co Cl (NH$_3$)$_5$]Cl$_2$) which separated out after an hour were filtered off. To the filtrate we then added 1 g of sodium cholate and 1 g of cholic acid, refluxing the mixture continuously. Then, after about 2 hr, when the solution had began to change its color from red to purple, the reflux condenser was removed and the solution was gently heated on a water bath in order to evaporate the solvent gradually. After a while, a beautiful purple precipitate (Co chol$_2$·1.5cholH) was formed; when the purple color of the solution was changed to a light red-orange, the purple precipitate was filtered off. A large volume of ether was poured into the filtrate to precipitate pinkish products. Because they still contained a considerable amount of cholic acid, the crude products were dissolved into 50 m*l* of methanol; with the addition of 200m *l* of ether they were precipitated as a red-orange product which was then filtered, washed with ether, and dried in air. For further purification, the product was reprecipitated with acetone. Yield, 0.2 g (6%).

Found: Co, 4.18; C,[*1]; H, 9.48; NH$_3$, 6.21%.

Calcd: Co, 4.38; C,[*1]; H, 9.73; NH$_3$, 6.22%.

Red-orange powder, soluble in methanol and ethanol, insoluble in acetone, ether, and water.

8) Cholatopentaamminecobalt(III) Chloride, [Co chol(NH$_3$)$_5$]Cl$_2$. Into 200 m*l* of methanol we dissolved 0.6 g of [Co chol (NH$_3$)$_5$]chol$_2$. After 10 m*l* of water had then been added to the solution, a few drops of concentrated hydrochloric acid were added and the mixture was stirred vigorously; then an appropriate amount of ether was poured into the solution to form a red-orange precipitate. This precipitate was filtered off and dissolved into 200 m*l* of methanol again, then, after the water and the concentrated hydrochloric acid had been added as before, it was reprecipitated with ether, filtered, washed with ether several times, and dried in air. Yield, 0.2 g (73%).

Found: 9.71; C,[*1]; H, 8.39; NH$_3$, 13.05%.

Calcd: 9.47; C,[*1]; H, 8.74; NH$_3$, 13.65%.

Red-orange powder, soluble in water, methanol, and ethanol, and insoluble in acetone and ether.

9) cis-Dicholatobis(ethylenediamine)cobalt(III) Chloride, *cis*-[Co chol$_2$ en$_2$]Cl. In 60 m*l* of ethanol we suspended 0.65 g of *trans*-[Co Cl$_2$ en$_2$]Cl or *cis*-[Co Cl$_2$ en$_2$]Cl and 2 g of sodium cholate; the solution was gradually heated on a water bath, using a reflux condenser. After about 3 hr, the red solution produced was filtered to remove the unreacted materials, and then about 4 volumes of ether were poured into the filtrate to form a pale red precipitate, which was filtered off and washed with ether. The precipitation from ethanol solution with ether was repeated several times in order to purify it. Yield, 1.7 grams (66%).

Found: Co, 5.65; C,[*1]; H, 9.17; ,N 5.49%.

Calcd: Co, 5.73; C,[*1]; H, 9.20; N, 5.44%.

Pale red powder, very soluble in methanol, ethanol, *n*-butanol and anhydrous acetic acid, and insoluble in acetone and ether.

10) cis-Dicholatobis(ethylenediamine)chromium(III) Chloride, *cis*-[Cr chol$_2$ en$_2$]Cl. Prepared by the same method as that described under 9) using 0.6 g of *trans*-[Cr Cl$_2$en$_2$]Cl or *cis*-[Cr Cl$_2$ en$_2$]Cl and 2 g of sodium cholate. Yield, 1.5 g (63%).

Found: Cr, 4.79; C,[*1]; H, 9.17; N, 5.45%.

Calcd: Cr, 5.09; C,[*1]; H, 9.26; N, 5.48%.

Pale red powder, very soluble in methanol, ethanol, *n*-butanol, and anhydrous acetic acid, and insoluble in acetone and ether.

11) Tricholatotriamminecobalt(III), [Co chol$_3$ (NH$_3$)$_3$]. In a mortar we crushed 2.6 g of silver cholate, 0.4 g of [Co Cl$_3$ (NH$_3$)$_3$], and 0.3 g of cholic acid; the mixture was then warmed up to about 50°C by the use of hot air. Then a few drops of water was added to it, and the mixture was ground vigorously by the use of a pestle. After the bluish-green color of the mixture had turned

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9) P. Pfeiffer, P. Koch, G. Lando and A. Trieschmann, *Ber.*, **37**, 4255 (1904).

10) "Inorganic Syntheses," Vol. 2 (1946), p. 200.

[*1] The found values of carbon were always less than the calculated values; for example, [Co Cl (NH$_3$)$_5$]chol$_2$: Found 54.09; Calcd 57.09, [Co chol (NH$_3$)$_5$]chol$_2$: Found 56.78; Calcd 63.23, [Co chol (NH$_3$)$_5$]Cl$_2$: Found 38.77; Calcd 46.31, [Co chol$_2$ en$_2$]Cl: Found 55.29; Calcd 60.65, [Cr chol$_2$ en$_2$]Cl: Found 54.18; Calcd 61.07. It was found that a considerable amount of carbon was contained in the residue whenever the sample was burned. Because of the high carbon-to-metal atomic ratios in the complexes, carbide or carbonate may be produced when they were burned.

to red-violet and the reaction was over, a soluble part was extracted from the mixture with 50 m*l* of ethanol and the insoluble silver chloride was filtered off. The red-violet precipitate which appeared as the appropriate amount of ether was poured into the filtrate was filtered, washed with ether, and dried in air. The product was reprecipitated twice from an ethenol solution with ether. Yield, 1.5 g (67%).

Found: Co, 4.56; C, 64.08; H, 9.58; NH_3, 3.96%.

Calcd: Co, 4.43; C, 64.80; H, 9.47; NH_3, 3.83%. Red-violet powder, soluble in methanol and ethanol, and insoluble in acetone and ether.

Analysis. For the analysis of cobalt, the sample was first slowly burned with sodium hydrogensulfate in a crucible in order to change all the cobalt into $CoSO_4$, after which, the burned solid was dissolved into diluted hydrochloric acid. Then the cobalt was precipitated from the solution with α-nitroso-β-naphthol.

The chromium was determined as follows; the sample was decomposed, in a hot aqueous solution of sodium hydroxide, to chromium(III) hydroxide, which was oxidized by potassium peroxodisulfate to chromate(VI) ions, then, after the pH of the solution had been adjusted to 10, the intensities of the absorption at 348, 356, 388, and 396 mu were measured.

The nitrogen, carbon, and hydrogen were analyzed by ordinary microanalysis, except that the nitrogen which was contained as NH_3 was analyzed by Kjehldahl's method. The found values were in good agreement with the calculated values except in the case of carbon.

Infrared Absorption Spectra. The infrared absorption spectra were measured by Nujol mull method using a JASCO 301 (Japan Spectroscopic Co.) infrared spectrophotometer. The characteristic absorption maxima are listed in Table 1.

Visible and Ultraviolet Absorption Spectra. The visible and ultraviolet absorption spectra in solution were obtained with a Hitachi 139 spectrophotometer.

TABLE 1. INFRARED ABSORPTION MAXIMA OF COMPLEXES (cm^{-1})

	COO^- antisym. str.	N–H str.	O–H str.
[Co en_3]$chol_3$	1545	3195	3415
[Co chol $(NH_3)_5$]$chol_2$	1537	3290	3400 sh
[Co chol $(NH_3)_5$]Cl_2	1642	3190	3390 sh
[Co $chol_2$ en_2]Cl	1567	3265	3395
[Cr $chol_2$ en_2]Cl	1584	3250	3380
[Co $chol_3$ $(NH_3)_3$]	1560	3300	3400 sh
cholH	1712		

Results and Discussion

The authors succeeded in the preparation of various kinds of cholato-complexes, as has been described in the Experimental section. These are all red fine powders, insoluble in water and soluble in an organic solvent such as ethanol. We attempted to prepare [Cr chol $(NH_3)_5]^{2+}$ and [Cr-$chol_3$ $(NH_3)_3$] but neither of the pure products were obtained. For example, for the purpose of obtaining [Cr chol $(NH_3)_5]^{2+}$, when we employed method by which the corresponding cobalt complex had successfully been prepared, [Cr Cl $(NH_3)_5$]-$chol_2$ could be obtained, but further treatment was

TABLE 2. ABSORPTION MAXIMA OF COMPLEXES (Absorption maxima are given in cm^{-1} and intensities, log ε in parentheses)

Complex	I	II	III	IV	
[Co en_3] $chol_3$	21500 (1.94)	29400 (1.90)		46500 (4.15)	*
[Co en_3] Cl_3	21300 (1.94)	29470 (1.90)			
[Co chol $(NH_3)_5$] $chol_2$	19800 (1.88)	28400 (1.95)	42600 (3.90)	46500 (~3.94)	*
[Co chol $(NH_3)_5$] Cl_2	19800 (1.90)	28200 (1.99)	42500 (3.97)		*
[Co(CH_3COO)$(NH_3)_5$]$(ClO_4)_2$	19900 (1.88)	28400 (1.77)			4)
[Co $chol_2$ en_2] Cl	19600 (1.99)	~27500 (~2.0)	42500 (4.15)		*
cis-[Co($C_{17}H_{35}COO)_2en_2$] ClO_4	19800 (2.18)	27600 (1.98)			1)
[Cr $chol_2$ en_2] Cl	19500 (1.86)	26200 (1.66)	46000 (3.74)		*
cis-[Cr($C_{17}H_{35}COO)_2en_2$] ClO_4	19800 (1.99)	26600 (1.65)			1)
[Co $chol_3(NH_3)_3$]	19000 (1.85)	~27000	42600 (3.74)		*
fac-[Co($NH_2CH_2COO)_3$]	19200 (2.2)	26700 (2.14)			13)

* present work

not useful. That is, $[\mathrm{Cr\ Cl\ (NH_3)_5}]^{2+}$ was easily decomposed and a ligand-exchange reaction between $\mathrm{Cl^-}$ and $\mathrm{chol^-}$ was not performed smoothly. These phenomena are consistent with the fact that Co $\mathrm{chol_2}$ was produced as the cholatopentaamminecobalt(III) salt was prepared. A very small amount of an impure $[\mathrm{Cr\ chol_3\ (NH_3)_3}]$ was obtained by the reaction of Ag chol upon $[\mathrm{Cr\ Cl_3\ (NH_3)_3}]$ because of the incomplete reaction.

It was found that, in the reaction of $[\mathrm{Co\ Cl(NH_3)_5}](\mathrm{ClO_4})_2$ with Nachol, $[\mathrm{Co\ Cl\ (NH_3)_5}]\mathrm{chol_2}$ was first obtained, while in the case of $[\mathrm{M\ Cl_2en_2}]\mathrm{Cl}$ (M=Co, Cr) the ligand substitution took place immediately and a cholate was not prepared. This fact aroused our interest in its reaction mechanism.

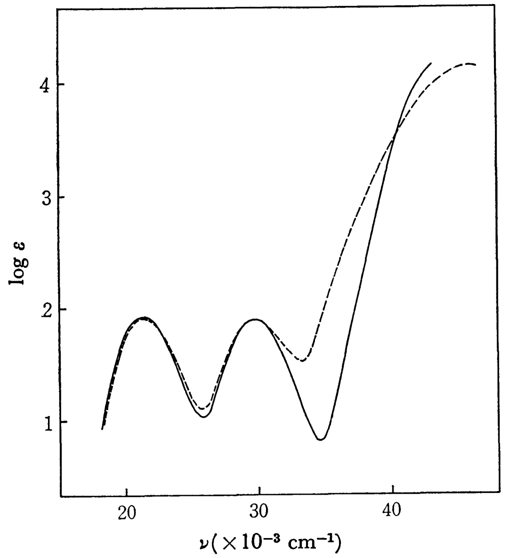

Fig. 2. Absorption spectra of trisethylendiamine complexes.
——— $[\mathrm{Co\ en_3}]\mathrm{Cl_3}$, ----- $[\mathrm{Co\ en_3}]\mathrm{chol_3}$

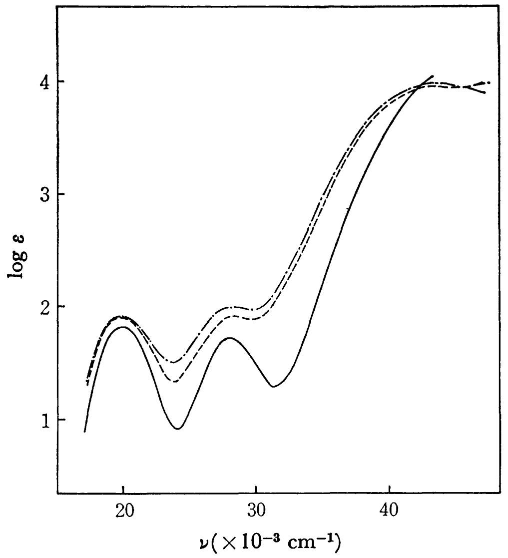

Fig. 3. Absorption spectra of monocholatocomplexes.
——— $[\mathrm{Co(CH_3COO)(NH_3)_5}]^{2+}$,*----- $[\mathrm{Co\text{-}chol(NH_3)_5}]\mathrm{chol_2}$, (in methanol), — — — $[\mathrm{Co\text{-}chol(NH_3)_5}]\mathrm{Cl_2}$ (in methanol).

* M. Linhard, M. Weigel, *Z. Anorg. Allg. Chem.*, **264**, 321 (1951).

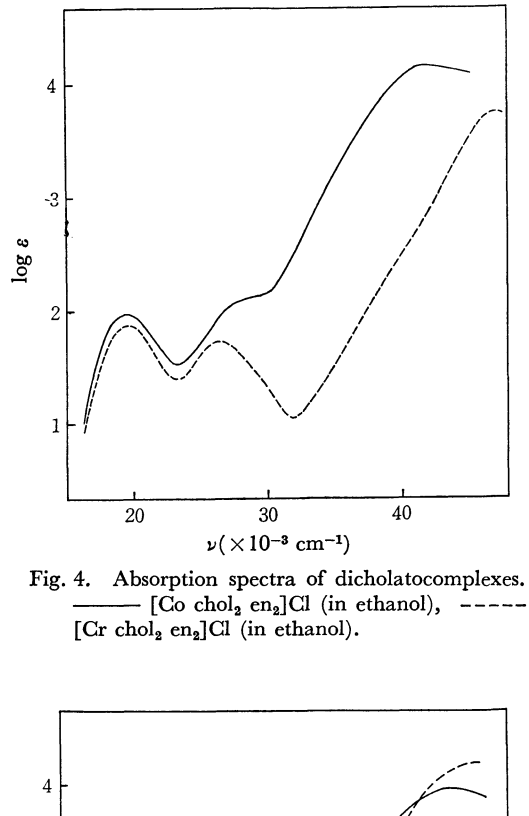

Fig. 4. Absorption spectra of dicholatocomplexes.
——— $[\mathrm{Co\ chol_2\ en_2}]\mathrm{Cl}$ (in ethanol), ----- $[\mathrm{Cr\ chol_2\ en_2}]\mathrm{Cl}$ (in ethanol).

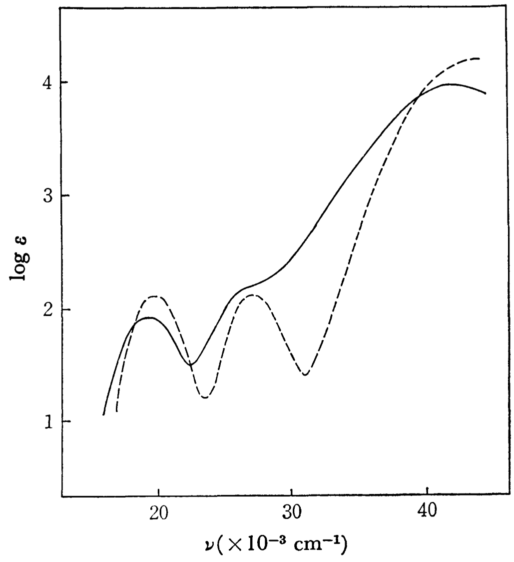

Fig. 5. Absorption spectra of tricholatocomplex.
——— $[\mathrm{Co\ chol_3\ (NH_3)_3}]$ (in ethanol), ----- *fac*-[Co gly₃].

As is shown in Table 2 and Figs. 2,3,4 and 5, each complex shows two spin-allowed bands which are characteristic of d^3 or low-spin d^6 complexes. An intense absorption band due to cholate ions was also seen in each case. The absorption band at 46500 cm^{-1} in [Co en_3]$chol_3$ coincides with the absorption band which is considered to be due to free cholate ions. Thus, in this case, the cholate ions are not at all coordinated. The spin-allowed bands of [Co en_3]$chol_3$ coincide with those of [Co en_3]Cl_3; this result confirmes that the compound must be a cholate salt of [Co en_3]$^{3+}$. However, in all the complexes except [Co en_3]$chol_3$ the cholate bands shifted to 42500 cm^{-1}; this shift suggests that it must be a specific absorption band of coordinated cholate ions. A similar result is also found in the case of [Co chol $(NH_3)_5$]$^{2+}$ (Fig. 3); either two ligand-field bands or a specific absorption band due to the cholate ion of [Co chol $(NH_3)_5$]$chol_2$ coincides well with that of [Co chol $(NH_3)_5$]Cl_2 in both the position and the intensity of the absorption maximum; furthermore, the absorption spectra of [Co chol $(NH_3)_5$] $chol_2$ have a band due to uncoordinated cholate ions at 46500 cm^{-1}, much like [Co en_3]-$chol_3$, while no such band is seen in [Co col $(NH_3)_5$]-Cl_2. The so-called "first" and "second" absorption bands of [Co chol $(NH_3)_5$]$^{2+}$ coincide with those of [Co (CH_3COO) $(NH_3)_5$]$^{2+}$ with respect to position and pattern. The intensity of the first band is slightly higher, and that of second band of [Co chol $(NH_3)_5$]$^{2+}$ is considerably higher, than that of the corresponding band of [Co (CH_3COO) $(NH_3)_5$]$^{2+}$. The increase in intensity in the case of the second band is evidently due to the overlap of the intense cholate band and the second band. Thus, the ligand-field bands of [Co chol $(NH_3)_5$]$^{2+}$ are essentially equal to those of [Co (CH_3COO)-$(NH_3)_5$]$^{2+}$, which means that the cholate ion coordinates to the cobalt through the carboxyl group.

The spin-allowed bands of [Co $chol_2$ en_2]Cl are similar to those of the corresponding *cis*-distearatocobalt(III)-complex. That is, the patterns and the positions of the absorption band of the two complexes agree well except for the intensity of the second absorption band of the cholato complex, which is again influenced by the specific absorption. Similarly, the absorption spectrum of [Cr $chol_2$ en_2]Cl is consistent with that of the corresponding complexes, [Cr $(C_{17}H_{35}COO)_2$ en_2]ClO_4, in position and pattern. These two cholato cobalt-(III) and chromium(III) complexes have the first absorption band characteristic of *cis*-diacido complexes. That is, the band does not show any splitting characteristic of *trans*-diacido-complexes. Thus, the complexes should have the *cis* structures.[11,12] The starting materials used here are [Co Cl_2 en_2]Cl and [Cr Cl_2 en_2]Cl respectively, and the *cis*- and *trans*- or complexes give the same product in each case. In other words, even though the *trans* complex is used as the starting material, the *cis* complex is obtained. The isomerisation reaction from *trans* to *cis* must take place. The situation is similar to the case of long-chain fatty acid complexes reported previously[2]; the reason for this isomerisation must be similar. That is, as the cholate ion is bulky, then the interaction between the cholate ion as ligand in this complex must strongly affect the *trans-cis* isomerisation reaction.

The absorption spectrum of [Co $chol_3$ $(NH_3)_3$] has two ligand-field bands and one specific absorption band (Fig. 5). The latter agrees well with the bands of the mono- and di-cholato complexes with respect to position. However, its intensity is fairly low, and its half-width is quite large. Moreover, there is a large shoulder on the longer-wavelength side of the specific absorption band. The specific absorption band covers the second absorption band and makes it obscure. The position of the maximum absorption of the second band was estimated to be at 27000 cm^{-1}, and the molar extinction coefficient was estimated to be about 100. These absorption bands agree with the absorption bands of *fac*-[Co $(NH_2CH_2COO)_3$], which possesses a similar *cis*-Co N_3O_3 configuration.[13] The complex obtained here should have a *fac*-configuration.

The infrared spectra are rather complicated in each case. However, many bands are associated with cholic acid. The characteristic absorptions are summarized in Table 1. It is observed that the absorptions assigned to the antisymmetric vibrations of COO^- are the considerably shifted to the lower-wave number side compared with the corresponding absorptions in free cholic acid. The absorption at 1537 cm^{-1} of [Co chol $(NH_3)_5$]$chol_2$ is fairly intense and has a small shoulder at 1640 cm^{-1} which is not listed in the table. Consequently, the absorption bands at 1537 cm^{-1} and 1545 cm^{-1} must be associated with the uncoordinated cholate ions in [Co chol $(NH_3)_5$]$chol_2$ and [Co en_3 $chol_3$] respectively. It is also found that the wave numbers of the COO^- antisymmetric vibration in the order; [Co chol $(NH_3)_5$]Cl_2, [Co $chol_2$ en_2]Cl, [Co $chol_3$-$(NH_3)_3$], and [Co en_3]$chol_3$. It is generally known that the absorption of a free carboxylic group should be at 1700—1730 cm^{-1} (in the free cholic acid at 1712 cm^{-1}), and that the absorption of a COO^- group coordinated to Co(III) or Cr(III) should be at 1620—1650 cm^{-1} and should be shifted to the lower-wave number side as the coordinate bond increases in ionic character.[14] These inter-

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[11] M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **267**, 121 (1951).

[12] Y. Shimura, This Bulletin, **25**, 49 (1925).

[13] Y. Shimura and R. Tsuchida, *ibid.*, **29**, 311 (1956).

[14] K. Nakamoto, "Spectroscopy and Structure of Metal Chelate Compounds," John Wiley & Sons, New York (1960), p. 277.

pretations were supported by the above results. That is, in the free cholic acid the maximum is at 1712 cm^{-1}; in the monocholato complex, at 1642 cm^{-1}; in the dicholato complex, at 1567 cm^{-1} (Co complex) and at 1584 cm^{-1} (Cr complex), and in the tricholato complex, at 1569 cm^{-1}. The absorption maxima of the monocholato complex are comparable with those of the monoacetato complexes. However, when there is such a large steric hindrance on the *cis* configuration as *cis*-dicholato and *fac*-tricholato complexes, the Co-O bond length may be lengthened by the hindrance and ionic character of the bonds may increase.