BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1848—1854 (1967)

Systematic Synthesis of Ammine Series of Chromium(III) Complexes*1

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(Received October 19, 1966)

The systematic synthesis of ammine series of chromium(III) complexes has been developed by using aquopentamminechromium(III) nitrate as a starting material. The procedure for the preparation of aquopentamminechromium(III) nitrate was improved to increase the yield. Twenty five sorts of chromium(III) complexes were obtained by the systematic synthesis, of which the procedures for the preparation of eleven sorts of complexes including a new complex, dinitrito-tetramminechromium(III) bromide, are described. The visible and ultraviolet absorption spectra in aqueous solutions and infrared spectra in solid state of those complexes have been obtained and their structures are discussed.

A general method for the preparation of Werner complexes seems to have made no striking progress after the Werner's age. He and chemists in his age established the proper synthetic processes for each of many complexes. Those processes, however, had no correlation to each other. Since 1956, a significant advance has been made in the field of the systematic synthesis of cobalt(III) complexes, which is composed of the successive and gradual substitution of tricarbonatocobaltate(III) ion, $[Co(CO_3)_3]^{3-}$.[1,2] In addition, another systematic synthesis has been found for oxalatocobalt(III) complexes.[3] However, such techniques for the preparations of other metal complexes are not particularly common yet. Dwyer[4] suggested that it is difficult to apply the methods which are used for the systematic synthesis of cobalt(III) complexes to the synthesis of chromium(III) complexes because of the different properties of chromium(III) from those of cobalt(III). One of the characteristics of chromium(III) is an ability to react in a wide range of pH with water molecules which are present as solvent. Besides, chromium(III) ions tend to form by olation a bridged hydroxo complex, a polynuclear complex. Recently, many important informations on the preparation of metal complexes have been accumulated from the studies on the reaction rate and mechanisms in solutions and those on the crystalline structure and the characteristics of coordination bond in solid state. Therefore, it seems interesting and worthwhile to investigate further the systematic synthesis of chromium(III) complexes on the basis of those informations.

*1 A part of this paper was presented at the 15th Annual Meeting of The Chemical Society of Japan, Kyoto, April, 1962.

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1) M. Mori, M. Shibata, E. Kyuno and T. Adachi, This Bulletin, **29**, 883 (1956).

2) M. Mori, M. Shibata, E. Kyuno and K. Hoshiyama, *ibid.*, **31**, 291 (1958).

3) F. P. Dwyer, I. K. Reid and F. L. Gavan, *J. Am. Chem. Soc.*, **83**, 1825 (1961).

4) F. P. Dwyer, "Advances in the Chemistry of the Coordination Compounds (Proceeding of Sixth International Conference on Coordination Chemistry)," ed. by S. Kirschner, Macmillan Co., New York (1961), p. 21.

The present paper is concerned with the systematic synthesis of ammine-series of chromium(III) complexes. In addition, the visible and ultraviolet absorption spectra in aqueous solution and the infrared spectra in solid state of the chromium(III) complexes which were newly measured are presented and the structures of these complexes are discussed.

Fundamental Idea of the Present Method

The important features of a systematic synthesis of ammine series of chromium(III) complexes consist of the successive substitutions of coordinated water molecules and oxalate groups by appropriate molecules or ions required for the ligand; the substitution reaction takes place by the thermal decomposition as well as the reaction in aqueous solutions.

Aquopentamminechromium(III) nitrate had been used as a starting material for the preparation of pentammine complexes. However, the yield of aquopentamminechromium(III) nitrate was not satisfactory from the stand-point that the compound was a starting material for the preparation of various chromium(III) complexes. The increase in yield of the compound was first undertaken; it was attained by improving the Mori's method, that is, by adding active charcoal.

Tetrammine complexes were prepared from oxalatotetramminechromium(III) nitrate which was obtained by the reaction of aquopentamminechromium(III) nitrate with oxalic acid and potassium oxalate. Since the oxalato complexes were easily converted into haloaquo complexes by the reaction with concentrated hydrohalogenic acid under suitable conditions, they were very useful in the preparation of desired complexes containing other ligands. A new compound, dinitritotetramminechromium(III) bromide, was prepared by this method.

These methods have been extended to a systematic synthesis of chromium(III) complexes such as series of oxalatoethylenediamine,[5] oxalatopropylenediamine[5] and oxalato-2, 2′-dipyridyl,[6] of which a few new nitrito, isothiocyanato and oxalato complexes were obtained from the corresponding haloaquo-complexes.

Experimental

Measurements of Visible and Ultraviolet Absorption Spectra. The visible and ultraviolet absorption spectra of all the complexes prepared were obtained by using a Hitachi EPS automatic recording spectrophotometer with quartz cells in aqueous solutions. Solutions (2 or 5×10^{-3} M) of the complexes were prepared by heating them gently on a water bath or by shaking them at room temperature in order to dissolve completely the samples except for nitrito complexes which were all dissolved in a cold water bath at about 5°C.

Wave numbers and molar extinction coefficients of absorption maxima of the products were calculated from each of the spectral charts of the samples.

Measurements of Infrared Absorption Spectra. Infrared absorption spectra of these compounds were measured by using a Hitachi EPI-2 and a Hitachi EPI-2G infrared spectrophotometer. In both cases, the potassium bromide disk and the Nujol mull methods were employed.

Analysis. The micro analysis of nitrogen was carried out by means of the Duma's method. The Volhard-Drechesel's method was used for the determination of halogen in the compound. To determine chromium content, the sample was fused with an excess of potassium hydroxide and chromium(III) was converted to potassium chromate, which was determined by the spectrophotometric method.

In addition, the samples were subjected to the thermogravimetric and the polarographic measurements*3 for the purpose of examining their purities.

Synthesis. *1) Aquopentamminechromium(III) Nitrate:* $[Cr(H_2O)(NH_3)_5](NO_3)_3$. Fine powdered chromium alum (100 g; 0.11 mol) and ammonium nitrate (300 g; 3.75 mol) were dissolved in 28% ammonia water (270 m*l*), and 2 g of active charcoal (dried at 120°C for 2 hr) were added as catalyser. The mixture was warmed on a water bath at 52°C for an hour with stirring. After cooling, it was filtered and the filtrate was poured slowly into cold dilute nitric acid (100 m*l* of water and 350 m*l* of nitric acid). If this procedure is not carried out at temperature within 20 to 27°C, the yield may be extremely decreased. When the solution was cooled by ice-water over 2 hr, brightly orange-yellow crystals began to be deposited out. The crystals were filtered and washed several times with a little amount of mixture of water and ethanol (1 : 1), then ethanol and ether. Since the raw product obtained in this way was always contaminated with active charcoal, it was necessary to recrystallize it by the Mori's method[7] except for using it as a starting material. Yield, 35 to 40 g (about 55%).

Found: Cr, 15.22; N, 32.81%. Calcd for $[Cr(H_2O)(NH_3)_5](NO_3)_3$: Cr, 15.24; N, 32.84%.

The corresponding chloride, bromide and iodide were prepared by adding a large excess of the corresponding sodium or potassium halide into the solutions of the nitrate. Since the products obtained were sometimes contaminated with nitrate, it may be necessary to purify them by recrystallization from the warm water containing the relevant anion. This is an improved method of Mori's.[7]

5) E. Kyuno, M. Kamada and N. Tanaka, unpublished.

6) The details of the synthesis of these series will be published elsewhere.

*3 Usually, it has been found that the half-wave potentials of polarographic reduction wave of chromium(III) complexes are different from each other in connection with the wave numbers of maxima of the first absorption band of those complexes. (For example, see A. A. Vlček. *Discussions Faraday Soc.*, No. 26, 164 (1958).) Therefore, it was possible to some extent to detect the impurities.

7) M. Mori, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **74**, 253 (1953).

2) Fluoropentamminechromium(III) Nitrate: $[CrF(NH_3)_5](NO_3)_2 \cdot H_2O$. Aquopentamminechromium(III) nitrate (15 g; 0.044 mol) was added gradually to concentrated hydrofluoric acid (20 g) in a polystyrene beaker and placed on a water bath at 45 to 50°C for a few minutes. A small volume of nitrogen dioxide gas evolved, and the reaction mixture changed to a reddish-brown solution. After cooling quickly, ethanol (100 m*l*) was added slowly to this solution, which was kept for a day in a refrigerator. The fine pink crystals were filtered and washed with ethanol and ether. Since the raw product was contaminated with unchanged aquo complex, the recrystallization was necessary. Yield, about 7 g (53%). The crystals were dried and stored in a silica gel desiccator.

Found: Cr, 17.33; N, 32.81%. Calcd for $[CrF(NH_3)_5](NO_3)_2 \cdot H_2O$: Cr, 17.44; N, 32.88%.

The nitrate was converted to the perchlorate or the iodide by repeating recrystallization twice from sodium perchlorate or sodium iodide solutions. The other preparative method of this salt using NH_4HF_2 has also been known.[8]

3) Chloropentamminechromium(III) Chloride: $[CrCl(NH_3)_5]Cl_2$. Ammonium chloride (5 g) was added to the solution of aquopentamminechromium(III) nitrate which was prepared by dissolving the complex (10 g; 0.029 mol) into water (20 m*l*) at 50 to 60°C. After cooling, concentrated hydrochloric acid (10 m*l*) was added to the solution, and it was kept in an ice-bath for a while. The pink-yellow precipitates of the chloride containing an appreciable amount of unchanged nitrate were separated out upon the addition of ethanol (30 m*l*). The precipitates were filtered, washed well with ethanol and dried at room temperature. When the product was allowed to stand for about an hour at 120°C in an air oven, it was completely converted to the purple-colored chloropentamminechromium(III) chloride by the following reaction:

$$[CrH_2O(NH_3)_5]Cl_3 \xrightarrow{\simeq 120°C} [CrCl(NH_3)_5]Cl_2 + H_2O$$

The purple residue was purified by treating with a small amount of cold water. Yield, 5 g (71%).

It was recrystallized from the aqueous solution containing a small volume of hydrochloric acid and dried over calcium chloride.

Found: Cr, 21.30; N, 28.80%. Calcd for $[CrCl(NH_3)_5]Cl_2$: Cr, 21.36; N, 28.76%.

A preparative method of this salt in aqueous solutions has been known.[9]

4) Bromopentamminechromium(III) Bromide: $[CrBr(NH_3)_5]Br_2$. This complex was prepared by the same method as for the chloropentamminechromium(III) chloride. Yield, 70%.

Found: Cr, 13.70; N, 18.44%. Calcd for $[CrBr(NH_3)_5]Br_2$: Cr, 13.80; N, 18.58%.

Other preparative methods have been already reported.[10,11]

5) Oxalatotetramminechromium(III) Nitrate: $[Crox(NH_3)_4]NO_3 \cdot H_2O$. After aquopentamminechromium(III) nitrate (10 g; 0.029 mol) was dissolved in water (20 m*l*) below 70°C, potassium oxalate hydrate (2.5 g) and oxalic acid dihydrate (2.5 g) were added to the solution. The reaction mixture was kept on a water bath at 70°C for a few minutes. After a pink-yellow color of the solution began to change to an orange color, the solution was filtered quickly by suction, and cooled in an ice-bath. The reaction proceeded as follows:

$$[Cr(H_2O)(NH_3)_5](NO_3)_3 + KHC_2O_4 \longrightarrow [Crox(NH_3)_4]NO_3 + KNO_3 + NH_4NO_3$$

The red-orange crystals were filtered, washed first with 50% and then 95% ethanol, and ether in turn, and were dried over silica gel in a desiccator. Yield, 6 g (77%). The compound was recrystallized from 5 to 10% potassium nitrate solution.

Found: Cr, 18.50; N, 25.30%. Calcd for $[Crox(NH_3)_4]NO_3 \cdot H_2O$: Cr, 18.56; N, 25.13%.

The corresponding chloride and bromide of the complex could be prepared by means of the double decomposition of the above nitrate with sodium chloride and bromide, respectively. The products prepared by this method were often contaminated with a small amount of the unchanged nitrate, and therefore it was purified by repeating recrystallization twice from about 10% of the corresponding salt solutions. The other preparative method has been reported by Pfeiffer and Basci, who used $[Cr(OH)_2(H_2O)_2py_2]Cl$ as a starting material.[12]

6) Chloroaquotetramminechromium(III) Chloride: $[CrCl(H_2O)(NH_3)_4]Cl_2$. Oxalatotetramminechromium(III) nitrate (5 g) was dissolved in concentrated hydrochloric acid (20 m*l*) and heated with stirring on a water bath at 40 to 50°C. The orange color of the solution obtained changed to deep violet after a while, and then fine reddish violet precipitates were deposited out. The mixture was kept at the same temperature for another few minutes and then filtered hot quickly to prevent the contamination of oxalic acid which dissociated from the starting material. The dark purple crystals (reddish purple when viewed under the microscope) were washed several times with a small volume of cold dilute hydrochloric acid (1 : 1), then ethanol and ether, and dried over a silica gel. Yield, 2.5 g (57%).

Found: Cr, 21.20; N, 22.75%. Calcd for $[CrCl(H_2O)(NH_3)_4]Cl_2$: Cr, 21.27; N, 22.91%.

Usually, the product was recrystallized from a small volume of dilute hydrochloric acid (1 : 1). Another method for the preparation of this complex has been reported by Pfeiffer.[13]

7) Bromoaquotetramminechromium(III) Bromide: $[CrBr(H_2O)(NH_3)_4]Br_2$. This compound was prepared with the same procedure as for chloroaquotetramminechromium(III) chloride, using concentrated hydrobromic acid. The product obtained was washed with 10% hydrobromic acid, ethanol and ether. Yield, 3 g (45%).

Found: Cr, 13.59; N, 14.82%. Calcd for $[CrBr(H_2O)(NH_3)_4]Br_2$: Cr, 13.76; N, 14.83%.

As it is not very soluble in water, it precipitates always while the solution is kept hot. The purification of the compound was made by the aquation-anation procedure.

8) cis-Dichlorotetramminechromium(III) Chloride: $[CrCl_2(NH_3)_4]Cl$. Chloroaquotetramminechromium(III)

8) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **278**, 24 (1955).
9) O. T. Christensen, *J. prakt. Chem.*, **23**, 54 (1881).
10) O. T. Christensen, *ibid.*, **23**, 27 (1881).
11) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **265**, 49 (1951).
12) P. Pfeiffer and S. Basci, *Ber.*, **38**, 3592 (1905).
13) P. Pfeiffer, *ibid.*, **38**, 3549 (1905).

chloride (6 g; 0.025 mol) was kept for about 4 hr at 120 to 130°C in an air oven. The dehydration of this compound was completed when its reddish purple changed to violet. The reaction that took place may be expressed as:

$$[CrCl(H_2O)(NH_3)_4]Cl_2 \xrightarrow{120-130^\circ C} [CrCl_2(NH_3)_4]Cl + H_2O$$

The product was washed with a small volume of 10% hydrochloric acid, ethanol and ether in turn, and dried over silica gel in a desiccator. Yield, 5.0 g (88%).

Found: Cr, 28.00; N, 24.31%. Calcd for $[CrCl_2(NH_3)_4]Cl$: Cr, 27.38; N, 24.74%.

Another method of preparation of this complex has been found.[14]

9) cis-Dibromotetramminechromium(III) Bromide: $[CrBr_2(NH_3)_4]Br$. The procedure employed for the preparation of this compound was analogous to that used for the preparation of *cis*-dichlorotetramminechromium(III) chloride. In this case, however, the temperature of air oven must be kept at 120°C. Yield, about 82%.

Found: Cr, 15.01; N, 15.28%. Calcd for $[CrBr_2(NH_3)_4]Br$: Cr, 14.45; N, 15.57%.

This compound has been already known.[15]

10) Dinitritotetramminechromium(III) Bromide: $[Cr(ONO)_2(NH_3)_4]Br$. Bromoaquotetramminechromium(III) bromide (2 g; 0.0053 mol) was dissolved in water (15 m*l*) at 50°C. After cooling to 20°C, potassium nitrite (2 g; 0.024 mol) was added to it with shaking quickly, and the solution was kept to stand in a refrigerator for a day. The orange-yellow crystals were filtered and washed with a small amount of the mixture of ethanol-water (1 : 1), ethanol and ether in turn. Then, it was dried quickly over silica gel in a desiccator. Yield, 1.3 g. (84%).

Found: Cr, 17.72; N, 28.90; Br, 27.42%. Calcd for $[Cr(ONO)_2(NH_3)_4]Br$: Cr. 17.80; N, 28.78; Br, 27.36%.

The chloride was prepared in the same way as that for the procedure of the above bromide by using chloroaquotetramminechromium(III) chloride as a starting material.

Found: Cr, 21.03; N, 34.11; Cl, 14.80%. Calcd for $[Cr(ONO)_2(NH_3)_4]Cl$: Cr, 21.00; N, 33.94; Cl, 14.32%.

It is very soluble in water and virtually insoluble in non-polar organic solvents. It was carefully stored in a sealed glass tube in dark because it is very unstable against moisture and light.

11) Oxalatotetramminechromium(III) Dioxalatodiamminechromate(III): $[Crox(NH_3)_4][Cr(ox)_2(NH_3)_2]$. Aquopentamminechromium(III) nitrate (10 g; 0.029 mol) was dissolved in hot water (about 20 m*l*) and powdered potassium oxalate hydrate (6 g) was added. The corresponding oxalate salt obtained after a few minutes was pink-yellow powder. It was washed with a small volume of cold water, ethanol and ether, and dried in air. Yield, 6 g (62%).

Found: Cr, 15.41; N, 20.76%. Calcd for $[CrH_2O(NH_3)_5]_2(ox)_3$: Cr, 15.53; N, 21.01%.

When the complex prepared by the above method was heated in an air oven at 120°C for 3 to 4 hr, the violet powder of the complex salt which consisted of the desired cation and anion was formed. The process is presumably expressed as a thermal decomposition,

$$2[CrH_2O(NH_3)_5]_2(ox)_3 \xrightarrow[3-4\ hr]{120^\circ C} [Crox(NH_3)_4][Cr(ox)_2(NH_3)_2] + 2H_2O + 4\,NH_3$$

In this case, it was unable to isolate each of components as solid state, because a suitable procedure is not available yet. However, since it was necessary to prove the proportion of components, it was determined by isolating them by means of an ion exchange resin. Yield, 5 g (98%).

Found: Cr, 18.70; N, 14.79%. Calcd for $[Crox(NH_3)_4][Cr(ox)_2(NH_3)_2]$: Cr, 18.37; N, 14.84%.

This salt was also able to be prepared from concentrated aqueous solutions of $K[Cr(ox)_2(NH_3)_2]\cdot H_2O$[16] and $[Crox(NH_3)_4]NO_3$.

Results and Discussion

A flow chart on the systematic synthesis of ammine series of chromium(III) complexes is given in Fig. 1.

Figure 1 shows that the skeleton of the systematic synthesis is constructed with several oxalato complexes and also expanded to the preparation of a new dinitrito complex. It is important that the direct reaction of concentrated hydrohalogenic acid with oxalato complex results in the formation of haloaquo derivatives under mild conditions. All haloaquo complexes in this case seem to have a cis form, because when two ligands substitute one coordinated oxalate ion, they are expected to occupy the cis position to each other as in the case of dinitritotetramminechromium(III) salt. It is also interesting to consider that the series of cis form can be derived from oxalato complexes. On the other hand, the further extended work on the investigation of the possibilities of the formation of *trans*-form has not been made owing to some difficulties. However, some new informations concerning the preparative procedures of trans series can be obtained from the above work.

The systematic synthesis of the diammine series from trioxalatochromium(III) ions by means of gradual substitution with ammonia ligand under suitable conditions was not successful because of lack of ability of its substitution in aqueous solutions.

The visible and ultraviolet absorption spectra of the complexes prepared by these procedures are listed in Table 1, although most of these spectra have been already reported by several

14) "Gmelins Handbuch der Anorganischen Chemie," 8 Auflage, Chrom, Teil C, Verlag Chemie, Weisenheim (1965), p. 178.

15) H. I. Schlesinger and D. N. Rickles, *J. Am. Chem. Soc.*, **51**, 3523 (1929).

16) A. Werner, W. J. Bowis, A. Hoblick, H. Schwarz and H. Surber, *Ann.*, **406**, 261 (1914).

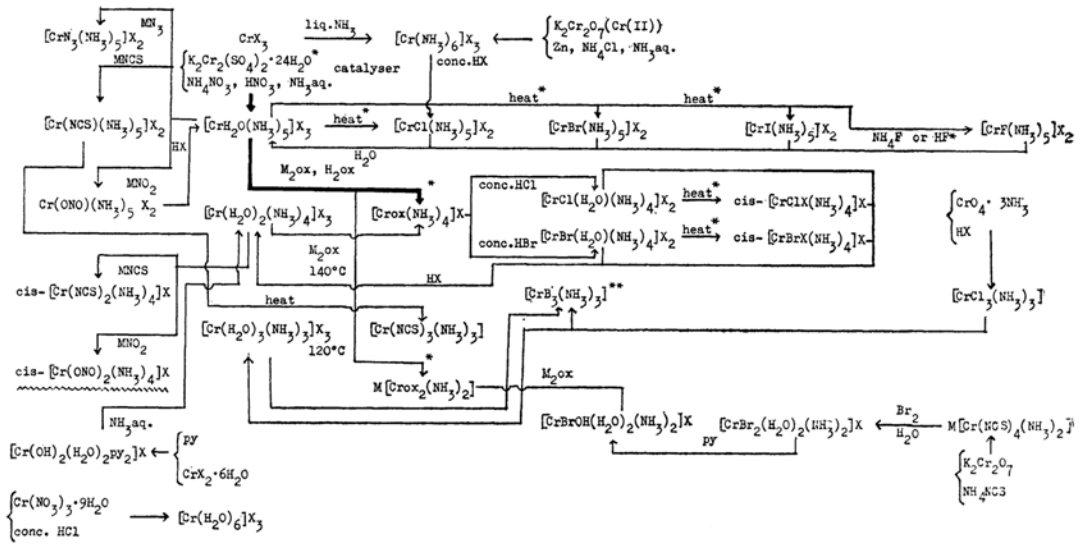

Fig. 1. Systematic synthesis of ammine series of chromium(III) complexes.

*, improved procedure, ——, main route; ~~~, new complex compound.
, M. Nakahara, This Bulletin **35, 783, 786 (1962).
B, appropriate ligand; ox oxalate; py, pyridine

TABLE 1. ABSORPTION MAXIMA AND INTENSITY OF AMMINE SERIES OF CHROMIUM(III) COMPLEXES

Complex	ν_1*	log ε_1	ν_2*	log ε_2	ν_3*	log ε_3	ν_4*	log ε_4	Literatures for earlier data
$[Cr(NH_3)_6]Cl_3$	21.55	1.62	28.49	1.57					12, 18
$[CrH_2O(NH_3)_5](NO_3)_3$	20.41	1.83	27.47	1.78	33.22	1.82			19, 20
$[CrF(NH_3)_5](NO_3)_2 \cdot H_2O$	20.00	1.63	27.03	1.34					
$[CrCl(NH_3)_5]Cl_2$	19.25	1.58	26.32	1.56					12
$[CrBr(NH_3)_5]Br_2$	19.16	1.58	26.35	1.57					12
$[CrI(NH_3)_5]I_2$	18.59	1.72			33.50	3.65			12
$[Cr(ONO)(NH_3)_5]Cl_2$	20.73	1.63	28.06	1.90					21
$[Cr(NCS)(NH_3)_5](NCS)_2$	20.41	1.84	27.03	1.68	33.78	3.47			21, 22
$[CrN_3(NH_3)_5](NO_3)_2$	20.07	2.16	26.18	1.97	38.00	3.70			21
$[Crox(NH_3)_4]NO_3 \cdot H_2O$	20.00	1.76	26.67	1.85					
$[Cr(ONO)_2(NH_3)_4]Cl$	20.24	1.90	27.68	2.10					
cis-$[Cr(NCS)_2(NH_3)_4]NCS$	20.16	1.92	26.88	1.74	33.11	3.71	38.46	3.62	
$K[Cr(ox)_2(NH_3)_2] \cdot H_2O$	18.69	1.89	26.67	1.85			37.74	3.32	
$NH_4[Cr(NCS)_4(NH_3)_2]\frac{2}{3}H_2O$	19.05	1.96	25.64	1.89	33.11	4.09	43.48	4.29	23

* ν_n is wave number of nth absorption maximum.

workers.[11,17-21] The results obtained in this study may be more accurate than those given in the earlier papers[17,21].

The absorption spectra of all oxalato complexes are given in Fig. 2. Figure 2 shows that the wave numbers of the absorption maxima decrease in the order, $[Cr(NH_3)_6]^{3+} > [Crox(NH_3)_4]^+ > [Cr(ox)_2(NH_3)_2]^- > [Cr(ox)_3]^{3-}$. The wave numbers for the first absorption band of the complexes belonging to each series are plotted in Fig. 3 in the same way as in the case of cobalt(III) complexes.[2] All the plots are given on a line only except for $[Cr(ox)_2(NH_3)_2]^-$ which is located below the line, as seen in Fig. 3.

Dioxalatodiamminechromate(III) ion, $[Cr(ox)_2(NH_3)_2]^-$, must have two geometrical isomers.

17) J. Bjerrum and C. G. Lamm, *Acta Chem. Scand.*, **9**, 216 (1955).
18) C. E. Schäffer, *J. Inorg. Nucl. Chem.*, **8**, 149 (1958).
19) M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63**, 327 (1959).
20) M. Linhard, H. Siebert and M. Weigel, *Z. anorg. Chem.*, **278**, 287 (1955).
21) R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 471 (1938).

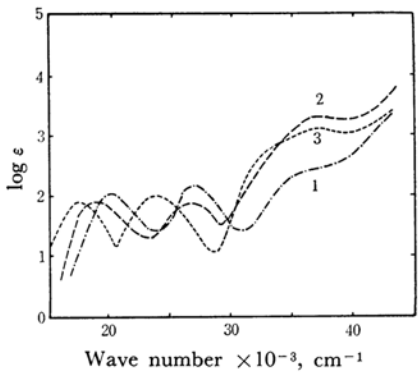

Fig. 2. Absorption spectra of oxalatoamminechromium(III) complexes: (1) $[Crox(NH_3)_4]NO_3 \cdot H_2O$, (2) $K[Cr(ox)_2(NH_3)_2] \cdot H_2O$ and (3) $K_3[Cr(ox)_3] \cdot 3H_2O$.

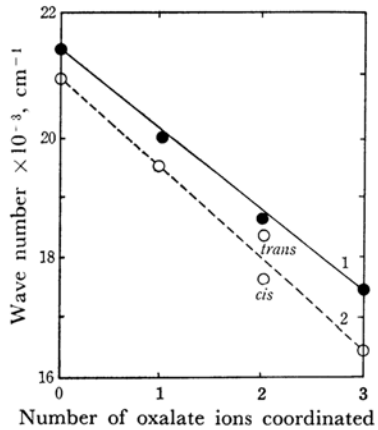

Fig. 3. The relation between wave numbers of the first absorption bands of oxalatoammine complexes and the number of oxalate ions coordinated: (1) oxalatoamminechrominum(III) series and (2) oxalatoamminecobalt(III) series.

which correspond to cis and trans forms in regard to the positions of two ammonia ligands. In the case of cobalt(III) complexes, it has been suggested that the first band of the trans isomer has a larger wave number than that of the corresponding cis isomer. If such a generalization can be extended to the above chromium(III) complex, it may be the cis-form, and another trans-form has never been known yet. However, it is also interesting in connection with Reineck's salt,[22] which has been known as the trans form in the regard to two ammonia molecules in solid state.[23]

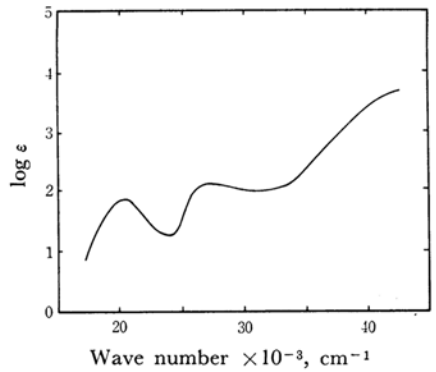

Fig. 4. Absorption spectra of $[Cr(ONO)_2(NH_3)_4]Cl$.

In this systematic synthesis, a new complex containing two nitrite ions as ligands was obtained by the procedure as shown in synthesis No. 10. As it was supposed that this complex is one of the structural isomers, *i. e.*, either dinitrotetramminechromium(III) or dinitritotetramminechromium(III), the structure of this complex was determined by the measurement of visible and infrared absorption spectra, which are shown in Fig. 4. It was found from Fig. 4 that the wave numbers for the first and the second absorption band of this complex agree with the dinitrito position but not the dinitro position in spectrochemical series, if the spectrochemical series in cobalt(III) complexes[24,25] is assumed to be applied to the corresponding chromium(III) complexes. Another support may be obtained from

Table 2. Infrared spectra of nitrito and nitro complexes in KBr disk method

Complex	Asym. NO str. cm^{-1}	Sym. NO str. cm^{-1}	References
$[Cr(ONO)_2(NH_3)_4]Cl$	1468	1035	
$[Cr(ONO)(NH_3)_5]Cl_2$	1465	1043	
$[Cr(ONO)(NH_3)_5]^{2+}$	1460	1048	26
$[Co(NO_2)(NH_3)_5]^{2+}$	1428	1310	26
trans-$[Co(NO_2)_2(NH_3)_4]Cl$	1427, 1408	1297	27
cis-$[Co(NO_2)_2(NH_3)_4]Cl$	1422, 1408	1299	27

22) P. Pfeiffer and M. Tilgner, *Z. anorg. Chem.*, **55**, 361 (1907).
23) Y. Takeuchi and Y. Saito, This Bulletin, **29**, 319 (1957).
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the fact that the pentamminechromium(III) complex with one nitrite ion coordinated has been known to exist as a nitrito complex, $[Cr(ONO)(NH_3)_5]^{2+}$, even in aqueous solutions.[21]

Another evidence was given by the measurement of infrared absorption spectra as shown in Fig. 5

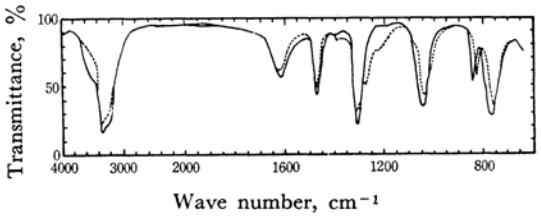

Fig. 5. Infrared spectra of nitritopentamminechromium(III) chloride (full line) and dinitritotetramminechromium(III) chloride (dotted line).

and Table 2, in which wave numbers of other nitrito and nitro complexes were listed. Stretching frequencies of this complex indicate that the ligand in this complex exists as the nitrito structure analogous to nitritopentamminechromium(III) salt[26] and trinitritotriamminechromium(III)[28]. From these results, the product which was prepared according to the above method was determined to be dinitritotetramminechromium(III) bromide.

The authors wish to thank Professor Ryokichi Tsuchiya of Kanazawa University for his helpful discussion, and the Ministry of Education and Japan Society for the Promotion of Science for the financial support granted for this research.

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