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# Preparation and Solid-phase Thermal Reactions of Hexaamminechromium(III) Amino Polycarboxylates under Quasi-isothermal and -isobaric Conditions1)

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The following hexaamminechromium(III) amino polycarboxylates were prepared: $[Cr(NH_3)_6]Naedta \cdot 3H_2O$, $[Cr(NH_3)_6]Napdta \cdot 6H_2O$, $[Cr(NH_3)_6]HK_3Cl(nta)_2 \cdot 2H_2O$ and $[Cr(NH_3)_6]KCl(nta) \cdot 2H_2O$, where edta, pdta and nta denote ethylenediaminetetraacetate, propylenediaminetetraacetate and nitrilotriacetate ions, respectively. Their thermal reactions in the solid-phase were examined by Q-derivatography (quasi-closed system; quasi-isothermal and -isobaric conditions) and D-derivatography (open system; dynamic conditions). The reactions in open system were too complicated to yield uniform intermediates. On the other hand, each reaction step in the quasi-closed system was definite and reproducible, the products obtained in each reaction step being remarkably pure.

Studies on the thermal reactions of metal complexes in the solid-phase have mostly been carried out in the open system.2) Two inherent problems have frequently been encountered, (a) difficulty of keeping the desired temperatures uniform over all parts of the sample, (b) change in the results caused by experimental conditions such as type of instrument, amount of sample, heating rate *etc.*

Recently, a new thermoanalytical instrument (Q-derivatograph) was developed, with which thermal reactions of samples can be followed under quasi-isothermal and -isobaric conditions.3) We studied the thermal reactions of hexaamminechromium(III) amino polycarboxylates under Q- and D-conditions4) and found that the results obtained under Q-conditions are reproducible and the intermediates in each reaction step can be obtained remarkably pure.

The present study was undertaken (1) to prepare the hexaamminechromium(III) amino polycarboxylates, (2) to observe the thermal reactions of the complexes under Q-conditions together with those under D-conditions, and (3) to test the possibility of synthesis of amino polycarboxylato-complexes by using the thermal reactions in the solid-phase.

Edta, pdta, and nta ions, which denote ethylenediaminetetraacetate, propylenediaminetetraacetate and nitrilotriacetate ions, respectively, were chosen mainly because of the expectation that the products obtained upon heating could be identified with certainty by referring to the well-known chromium(III) complexes containing these agents.

## Experimental

*Preparation of Complexes. Hexaamminechromium(III) Sodium Ethylenediaminetetraacetate Trihydrate,* $[Cr(NH_3)_6]Naedta \cdot 3H_2O$. Fifteen grams (50 mmol) of $H_4edta$ was dissolved in a solution of NaOH (8 g, 20 mmol) in 50 cm$^3$ of water. The solution was then added to a solution of $[Cr(NH_3)_6]Cl_3$ (13 g, 50 mmol) in 50 cm$^3$ of water. The resulting mixture was allowed to stand for a few days in a refrigerator, 18 g of yellow well-defined crystals being obtained and recrystallized from water.

Found: C, 22.82; H, 7.25; N, 21.21%. Calcd for $C_{10}H_{36}N_8O_{11}CrNa$: C, 23.12; H, 6.99; N, 21.57%.

*Hexaamminechromium(III) Sodium Propylenediaminetetraacetate Hexahydrate,* $[Cr(NH_3)_6]Napdta \cdot 6H_2O$. Sixteen grams (50 mmol) of $H_4pdta$ was dissolved in a solution of NaOH (8 g, 20 mmol) in 70 cm$^3$ of water. The solution was then added to a solution of $[Cr(NH_3)_6]Cl_3$ (13 g, 50 mmol) in 50 cm$^3$ of water, to which *ca.* 10 cm$^3$ of ethanol was gradually added. The resulting mixture was allowed to stand for several days in a refrigerator. 20 g of the products was thus obtained, which was recrystallized from water. The color of the samples containing $[Cr(NH_3)_6]$ cation was yellow irrespective of the anions involved.

Found: C, 22.39; H, 7.66; N, 19.11%. Calcd for $C_{11}H_{44}N_8O_{14}CrNa$: C, 22.49; H, 7.55; N, 19.07%.

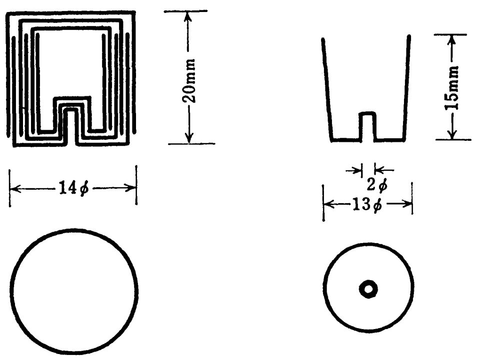
*Hexaamminechromium(III) Hydrogen Tripotassium Chloride Bis(nitrilotriacetate) Dihydrate,* $[Cr(NH_3)_6]HK_3Cl(nta)_2 \cdot 2H_2O$. $H_3nta$ (19 g, 100 mmol) was added to a solution of $[Cr(NH_3)_6]Cl_3$ (13 g, 50 mmol) in 150 cm$^3$ of water. The slurry was continuously stirred under ice-cooling, aqueous KOH being added drop by drop in amounts enough to dissolve the $H_3nta$ and to obtain a solution of pH 8. To this was added *ca.* 10 cm$^3$ of ethanol, and the resulting solution was left to stand for a week in a refrigerator. 18 g of plate-like crystals was obtained. Recrystallization was carried out as follows. The crystals were dissolved in a small amount of water, a small amount of ethanol then being added and the resulting solution kept standing in a refrigerator for about a week. Purified triangular plate-like crystals were obtained.

Found: C, 20.36; H, 5.55; N, 15.36%. Calcd for $C_{12}H_{35}N_8O_{14}ClCrK_3$: C, 20.01; H, 4.90; N, 15.56%.

At first, the composition of the compound could not be determined, but the following nitrilotriacetate ($[Cr(NH_3)_6]KCl(nta) \cdot 2H_2O$) was obtained. This differs considerably in property from the former compound; for example the former was somewhat acidic in water (pH 4—5), whereas the latter was slightly alkaline (pH 8—9). A comparison of analytical data, IR spectra and thermal behavior between them revealed that the above composition is valid for the former complex.

*Hexaamminechromium(III) Potassium Chloride Nitrilotriacetate Dihydrate,* $[Cr(NH_3)_6]KCl(nta) \cdot 2H_2O$. Ten grams (50 mmol) of $H_3nta$ was added to a solution of $[Cr(NH_3)_6]Cl_3$ (13 g, 50 mmol) in 150 cm$^3$ of water. To the mixture was added aqueous KOH drop by drop with continuous stirring under ice-cooling, the final pH of the solution being adjusted to 10. *Ca.* 10 cm$^3$ of ethanol was added to the resulting solution, which was kept standing in a refrigerator for a week, 12 g of the products being obtained. Recrystallization was carried out from water containing a small amount of ethanol. Octahedrally shaped crystals were obtained.

Found: C, 16.23; H, 6.12; N, 21.58%. Calcd for $C_6H_{28}$-



(a) Labyrinth crucible (b) Coverless crucible

Fig. 1. Pt crucibles employed in Q-derivatograph (a) and D-derivatograph (b).

$N_7O_8ClCrK$: C, 15.91; H, 6.23; N, 21.65%.

The presence of $K^+$ and $Cl^-$ was quantitatively determined by the use of $[Co(NO_2)_6]^{3-}$ and $Ag^+$ ions.

*Isolation of the Products Obtained in Each Thermal Reaction Step.* Temperature and heating time were determined from the data obtained under Q- and/or D-conditions.

*(1)* $NH_4[Cr(edta)]\cdot 2H_2O$ *from* $[Cr(NH_3)_6]Naedta\cdot 3H_2O$: $[Cr(NH_3)_6]Naedta\cdot 3H_2O$ (1 g, 2 mmol) was put in a labyrinth crucible (Fig. 1-(a)), and heated at 150 °C for 5 h in an air-bath. A violet product (Na[Cr(edta)]) obtained was dissolved in a small amount of water. $NH_4Cl$ (1 g, 16 mmol) was added and the solution was allowed to stand in a refrigerator for a few days, 0.5 g of violet crystals being obtained.

Found: C, 30.31; H, 5.25; N, 10.82%. Calcd for $C_{10}H_{20}N_3O_{10}Cr$: C, 30.47; H, 5.08; N, 10.66%.

Since the preparation of sodium salts was difficult, the products were purified as ammonium salts.

*(2)* $Na[Cr(pdta)]\cdot 3H_2O$ *from* $[Cr(NH_3)_6]Napdta\cdot 6H_2O$: One gram (2 mmol) of $[Cr(NH_3)_6]Napdta\cdot 6H_2O$ was charged in a labyrinth crucible and heated at 210 °C for one hour. Violet product (Na[Cr(pdta)]) thus obtained was dissolved in a small amount of water. Ethanol (one tenth of the whole volume) was added and the solution was allowed to stain in a refrigerator for about one week. 0.5 g of violet crystals were obtained.

Found: C, 30.42; H, 4.88; N, 6.45%. Calcd for $C_{11}H_{20}N_2O_{11}CrNa$: C, 30.64; H, 4.67; N, 6.50%.

*(3)* $Na_3[Cr(nta)_2]\cdot 5H_2O$ *from* $[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$: $[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$ (1.5 g, 2 mmol) was charged in a labyrinth crucible and heated at 135 °C for 3.5 h in an air-bath. A pink product ($K_3[Cr(nta)_2]$) was obtained, which was dissolved in water. The solution was passed through a column of Dowex 1-X8 (Cl-form) resin. The pink band was developed on the column, which was eluted with 0.4 mol $cm^{-3}$ NaCl solution. The effluent was then concentrated to one-third of its volume at about 30 °C on a rotary evaporator, and kept standing in a refrigerator overnight. 0.2 g of pink powdered crystals were obtained.

Found: C, 24.35; H, 2.60; N, 4.68%. Calcd for $C_{12}H_{17}N_2O_{17}CrNa_3$: C, 24.75; H, 2.94; N, 4.81%.

*(4)* $[Cr(nta)(NH_3)_2]KCl$ *from* $[Cr(NH_3)_6]KCl(nta)\cdot 2H_2O$: $[Cr(NH_3)_6]KCl(nta)\cdot 2H_2O$ (1 g, 2 mmol) was put in a labyrinth crucible and heated at 130 °C for 6.5 h in an air-bath. 0.75 g of reddish brown products was obtained, which could not be purified because of the absence of suitable solvents. The products were highly soluble and readily hydrolyzed in water, so purification from water failed. The KCl contained in the products could not be removed. The results of elemental analyses indicate that the composition of the products is substantially uniform. This is a typical example showing that the thermal reaction of the samples proceeds uniformly under Q-conditions. It has not yet been clarified whether the KCl in the products is present in the crystals ($[Cr(nta)(NH_3)_2]KCl$) or as the contaminants ($[Cr(nta)(NH_3)_2]+KCl$).

*Instruments.* The TG curves of the complexes were measured under Q- and D-conditions by using a Q-derivatograph[3)] and a D-derivatograph.[5)] Figure 1 shows the Pt crucibles employed in this study. In the case of D-derivatography, all the measurements were caried out at a heating rate of 1 °C $min^{-1}$, 0.5 g of the samples being used in a coverless Pt crucible (Fig. 1-(b)). In Q-derivatography, 0.5 g of the samples were taken into a labyrinth Pt crucible (Fig. 1-(a)).[3)] The crucible consists of three Pt cups and three Pt covers. They are joined alternately. The sample decomposes on heating, evolving gases. The gases first occupy the inside of the crucible. Excess gases go out from the crucible only when the inside pressure exceeds the outside pressure. Thus, the inside of the crucible fulfills the autogenerated quasi-isobaric condition. IR and UV spectra were measured with the same apparatus as employed previously.[6)]

## Results and Discussion

*TG Curves of* $CuSO_4\cdot 5H_2O$. $CuSO_4\cdot 5H_2O$ is used as a typical example to explain the difference in the results obtained under Q- and D-conditions. Figure 2 shows the TG curves measured under Q-conditions (broken line) and D-conditions (solid line). A general TG pattern measured under D-conditions, often influenced by experimental conditions such as instruments employed, sample amount and heating rate, is shown. Stepwise dehydration is distinctly detectable under Q-conditions. The TG pattern was not influenced by experimental conditions. Figure 3 shows the relationship between dissociation pressure ($p$) and temperature ($T$) in $CuSO_4\cdot 5H_2O$.[7)] The first, second and third dehydration steps under one atmosphere are 102, 108 and 227 °C, respectively, close to the temperature (103, 114 and 230 °C) obtained under Q-conditions (Fig. 2). This indicates that under Q-conditions each dehydration step proceeds in a monovariant system and pure intermediates are obtainable in each plateau.

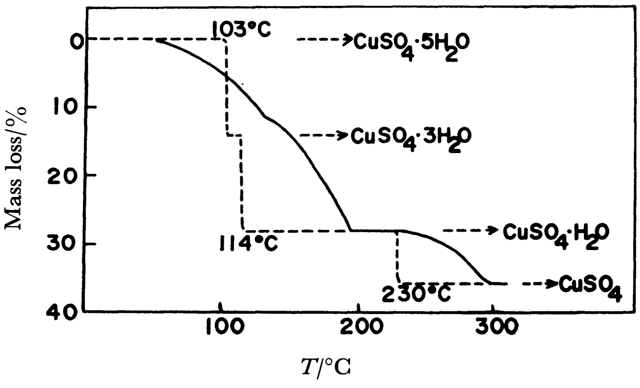


Fig. 2. TG curves of $CuSO_4\cdot 5H_2O$ measured under Q-(-----) and D-conditions (——).

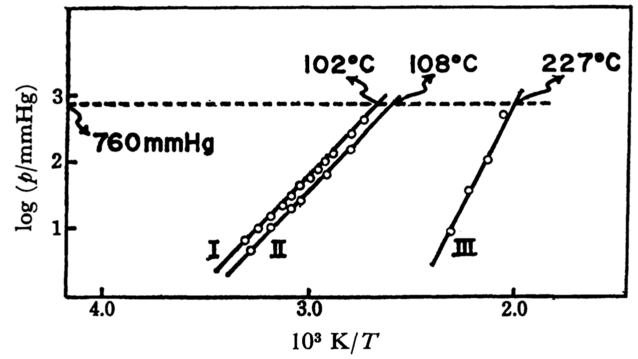


Fig. 3. Relationships between dissociation pressures ($p$) and temperatures ($T$) in $CuSO_4\cdot 5H_2O$.
I. $CuSO_4\cdot 5H_2O \rightleftharpoons CuSO_4\cdot 3H_2O+2H_2O$
II. $CuSO_4\cdot 3H_2O \rightleftharpoons CuSO_4\cdot H_2O+2H_2O$
III. $CuSO_4\cdot H_2O \rightleftharpoons CuSO_4+H_2O$

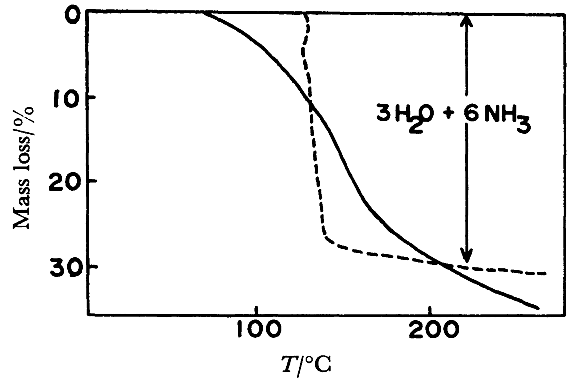


Fig. 4. TG curves of $[Cr(NH_3)_6]Naedta\cdot 3H_2O$ measured under Q-(-----) and D-conditions (——).

*TG Curves of the Complexes.* *$[Cr(NH_3)_6]Naedta\cdot 3H_2O$*: Figure 4 shows the TG curves of $[Cr(NH_3)_6]$-$Naedta\cdot 3H_2O$. Under D-conditions (solid line), the complex begins to decompose at *ca.* 70 °C and gradually loses the weight of $(3H_2O+6NH_3)$ up to about 200 °C; no plateau is detectable. Under Q-conditions (broken line), the complex suddenly loses weight at 130 °C and decomposes nearly isothermally, *viz.*, the complex evolves the gases $(3H_2O+6NH_3)$ in a narrow temperature range (130—140 °C), after which a clear plateau is obtained in the TG curve. At this stage, the original yellow complex turned violet, indicating that the edta anion in outer-sphere is coordinated to Cr(III) ion upon heating. From the results, 150 °C for 5 h was selected as the optimal heating conditions for obtaining $Na[Cr(edta)]$ from $[Cr(NH_3)_6]Naedta\cdot 3H_2O$.

*$[Cr(NH_3)_6]Napdta\cdot 6H_2O$*: The TG curve of the compound under D-conditions (Fig. 5) is essentially similar to that of the foregoing edta salt: the compound evolves the gases $(6H_2O+6NH_3)$ at 50—200 °C and then decomposes gradually. Under Q-conditions, the complex begins to decompose at 80 °C, the weight loss up to 20 wt% taking place nearly isothermally and reaching a plateau at *ca.* 200 °C. The coloration turned from yellow to violet at this plateau, from which the optimal condition for obtaining $Na[Cr(pdta)]$ from $[Cr(NH_3)_6]Napdta\cdot 6H_2O$ was selected as 200 °C for 1 h.

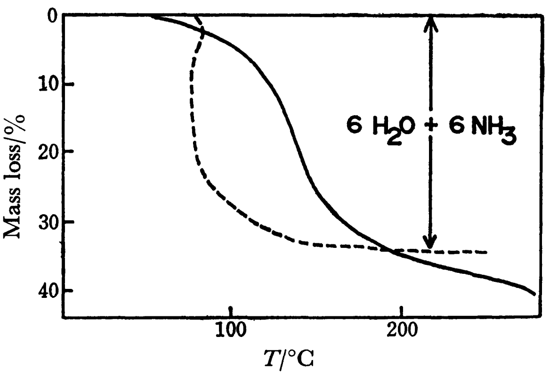


Fig. 5. TG curves of $[Cr(NH_3)_6]Napdta\cdot 6H_2O$ measured under Q- (-----) and D-conditions (——).

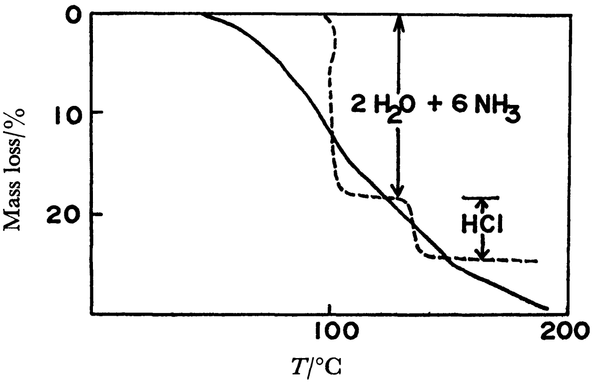


Fig. 6. TG curves of $[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$ measured under Q- (-----) and D-conditions (——).

It should be noted that the complex melts in its own crystalline water at the begining of the reaction under Q-conditions. A slight temperature drop appearing immediately after the weight loss begins is probably due to melting of the sample.

*$[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$*: The TG curves of $[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$ are shown in Fig. 6. The salt continues to decompose monotonously from 45 °C under D-conditions (solid line), no plateau being obtained in the TG curve. In contrast, two distinct plateaus are detectable under Q-conditions, one of which corresponds to the loss of the gases $(2H_2O+6NH_3)$ at 100—105 °C and the other to the loss of one mole of hydrogen chloride at 130—135 °C. The inintial yellow complex turned pink at the first plaueau, the coloration remaining unchanged at the second plateau. The change in coloration indicates that the complex is in turn converted into $K_3[Cr(nta)_2]HCl$ and then $K_3[Cr(nta)_2]$. The condition (135 °C for 3.5 h) is suitable for preparing $K_3[Cr(nta)_2]$ from $[Cr(NH_3)_6]$-$HK_3Cl(nta)_2\cdot 2H_2O$. $K_3[Cr(nta)_2]$ is readily hydrolyzed in water to yield $K[Cr(OH)(nta)(H_2O)]$,[8] but the situation is not so severe in the sodium salts and hence the thermal products were purified as sodium salts.

*$[Cr(NH_3)_6]KCl(nta)\cdot 2H_2O$*: The TG curve of the compound under D-conditions starts to fall at about 50 °C without reaching plateau (Fig. 7). Under Q-conditions, the complex evolves the gases $(2H_2O+4NH_3)$ at 110—120 °C, a plateau being reached. The coloration turned from original yellow to reddish brown,

TABLE 1. IR DATA DUE TO THE C=O STRETCHING VIBRATIONS

| Complex | $\tilde{\nu}_{C=O}$/cm$^{-1}$ a) | | |
|---|---|---|---|
| | -COOH | -COO-Cr(III) | -COO- |
| $[Cr(NH_3)_6]$Naedta·$3H_2O$ (yellow) | | | 1580(vs, br) |
| $NH_4[Cr(edta)]\cdot 2H_2O$ (violet) | | 1650(vs, br) | |
| $[Cr(NH_3)_6]$Napdta·$6H_2O$ (yellow) | | | 1590(vs, br) |
| Na[Cr(pdta)]·$3H_2O$ (violet) | | 1650(vs, br) | |
| $[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$ (yellow) | 1715(s) | | 1590(vs, br) |
| $Na_3[Cr(nta)_2]\cdot 5H_2O$ (pink) | | 1640(vs, br) | 1593(s) |
| $[Cr(NH_3)_6]$KCl(nta)·$2H_2O$ (yellow) | | | 1580(vs, br) |
| $[Cr(nta)(NH_3)_2]$KCl (reddish brown) | | 1650(vs, br) | |

a) The terms s, vs and br denote strong, very strong and broad, respectively.

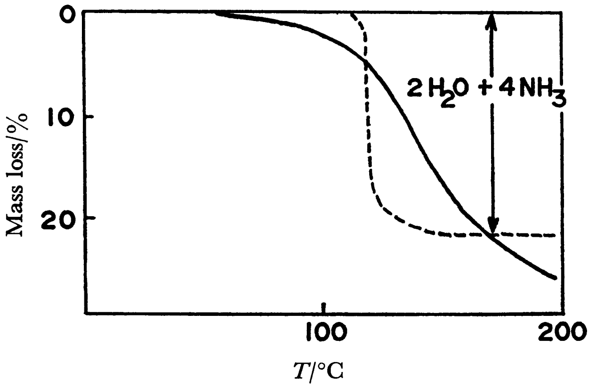


Fig. 7. TG curves of $[Cr(NH_3)_6]$KCl(nta)·$2H_2O$ measured under Q- (----) and D-conditions (——).

TABLE 2. ELECTRONIC SPECTRAL DATA DUE TO d-d TRANSITION ($\tilde{\nu}/10^3$ cm$^{-1}$)

| Complex$^{a)}$ | $\tilde{\nu}_I$(log $\varepsilon$) | $\tilde{\nu}_{II}$(log $\varepsilon$) |
|---|---|---|
| $[Cr(NH_3)_6]$Naedta·$3H_2O$ | 21.55(1.59) | 28.40(1.47) |
| $NH_4[Cr(edta)]\cdot 2H_2O$ | 18.40(2.33) | 25.45(2.07) |
| $[Cr(NH_3)_6]$Napdta·$6H_2O$ | 21.55(1.57) | 28.40(1.46) |
| Na[Cr(pdta)]·$3H_2O$ | 18.35(2.33) | 25.45(2.04) |
| $[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$ | 21.55(1.61) | 28.40(1.49) |
| $Na_3[Cr(nta)_2]\cdot 5H_2O$ | 19.87(1.64) | 27.84(1.47) |
| $[Cr(NH_3)_6]$KCl(nta)·$2H_2O$ | 21.55(1.59) | 28.40(1.47) |
| $[Cr(nta)(NH_3)_2]$KCl$^{b)}$ | 18.5 | 24.5 |

a) All the spectra were measured in water except for that of $[Cr(nta)(NH_3)_2]$KCl. b) The spectrum was measured by a diffuse reflectance method because the complex rapidly aquated in water.

indicating that the complex is converted into $[Cr(nta)(NH_3)_2]$KCl. Preliminary experiments showed that 130 °C for 6.5 h is the best condition for obtaining $[Cr(nta)(NH_3)_2]$KCl from $[Cr(NH_3)_6]$KCl(nta)·$2H_2O$. The products were highly soluble and rapidly hydrolyzed in water, purification from water thus being always unsuccessful.

*IR Data.* The IR data obtained from the C=O stretching vibrations utilized for determining the coordination modes of carboxylato groups are summarized in Table 1. IR spectral studies on the metal complexes containing amino polycarboxylates reveal that the bands due to free carboxylic acid (-COOH), coordinated carboxylate (-COO-Metal) and ionic carboxylate ($-COO^-$) appear at 1700—1740, 1620—1690 and 1550—1600 cm$^{-1}$, respectively.[9] $[Cr(NH_3)_6]$Naedta·$3H_2O$ and $[Cr(NH_3)_6]$Napdta·$6H_2O$ give the band at 1580 and 1590 cm$^{-1}$, respectively, indicating that both the edta and pdta ions are present in ionic form in the salts. The presence of the bands (1650 cm$^{-1}$) in $NH_4[Cr(edta)]\cdot 2H_2O$ and Na[Cr(pdta)]·$3H_2O$ suggests that the carboxylato groups in both the complexes are coordinated to Cr(III) ions. The appearance of the bands (1715 and 1590 cm$^{-1}$) in $[Cr(NH_3)_6]HK_3Cl(nta)_2\cdot 2H_2O$ indicates that the salt has free carboxylic acid and ionic carboxylato groups. The presence of both coordinated and ionic carboxylato groups in $Na_3[Cr(nta)_2]\cdot 5H_2O$ is supported by the bands at 1640 and 1593 cm$^{-1}$. The results also show that the nta ion in $[Cr(NH_3)_6]$KCl(nta)·$2H_2O$ is present in ionic form (1580 cm$^{-1}$), but that in $[Cr(nta)(NH_3)_2]$KCl is in coordinated form (1650 cm$^{-1}$).

*Electronic Spectral Data.* Electronic spectral data due to d-d transition obtained in water are given in Table 2. The first and second bands of the hexaamminechromium(III) complexes appear at 21.55 and 28.40 × $10^3$ cm$^{-1}$, respectively, irrespective of anions. The bands at 18.40 and 25.45 × $10^3$ cm$^{-1}$ in $NH_4[Cr(edta)]\cdot 2H_2O$ and 18.35 and 25.45 × $10^3$ cm$^{-1}$ in Na[Cr(pdta)]·$3H_2O$ resemble those of $[Cr(edta)(H_2O)]^-$ ion (18.4 and 25.5 × $10^3$ cm$^{-1}$).[10] This is due to the fact that both complexes are converted into [Cr(edta or pdta)$(H_2O)]^-$ ion in water. $Na_3[Cr(nta)_2]\cdot 5H_2O$ has bands at 19.87 and 27.84 × $10^3$ cm$^{-1}$, which are in the proximity of those of *trans*(N)-$(NH_4)_3[Cr(nta)_2]\cdot 4H_2O$ (20.0 and 27.8 × $10^3$ cm$^{-1}$).[8] The spectrum of $[Cr(nta)(NH_3)_2]$KCl was measured by a powder diffuse reflectance method since the complex is rapidly hydrolyzed in water. The bands at 18.5 and 24.5 × $10^3$ cm$^{-1}$ are substantially close to those of [Cr(nta)(bipy)] (18.6 and 24.6 × $10^3$) where bipy denotes 2,2'-bipyridine.[11] It seems that the chromium(III) ion in the products is surrounded by a $N_3O_3$ chromophore.

Study on the thermal reactions of $[Cr(NH_3)_6]X_3$ (X is a simple monodentate anion such as $Cl^-$, $Br^-$ and $I^-$) showed that the complexes undergo anation upon heating in open system and are successively converted into $[CrX(NH_3)_5]X_2$, $[CrX_2(NH_3)_4]$ and $[CrX_3(NH_3)_3]$.[12] It was found that under Q-conditions, even the complexes containing more complicated anions such as edta, pdta and nta ions undergo participation of these ions in the coordination sphere giving the corresponding amino polycarboxylato-complexes. The use of thermal reactions in the quasi-closed system would lead to the production of other new metal complexes, which do not seem to have been prepared in solutions.

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4) Throughout this paper, the terms Q-conditions and D-conditions are used to denote Quasi-isothermal and -isobaric conditions and Dynamic-conditions, respectively. In the quasi-closed system measurements are made by means of a Q-derivatograph and in the open system by means of a D-derivatograph.

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