BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2385—2392 (1968)

The Chromium(III) Complexes with Ammoniapropionicdiacetic Acid*[1]

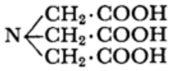
Akira UEHARA, Eishin KYUNO and Ryokichi TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

(Received February 5, 1968)

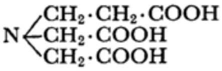
Ammoniapropionicdiacetic acid (APDA), which belongs to a group of chelating agents similar to that of ammoniatriacetic acid, was prepared. The newly-prepared complexes containing this chelating agent were as follows: $[Cr(OH)(apdaH)(H_2O)_2]$ (red purple) (I), $NH_4[Cr(OH)(apda)(H_2O)]\cdot 2H_2O$ (purple) (II), $(NH_4)_3[Cr(apda)_2]\cdot 2H_2O$ (pink) (III), $(Cr(apda)(bipy)]\cdot 3H_2O$ (brown) (IV), $[Cr(apda)(o\text{-phen})]\cdot 3H_2O$ (brown) (V), and $[Cr(apda)(py)_2]$(pink) (VI), where apda, bipy, *o*-phen, and py are the abbreviations of the ammoniapropionatediacetate ion, *o*-phenanthroline, 2,2′-bipyridyl, and pyridine respectively. On the basis of the chemical and thermal analyses, and on the basis of the measurements of the visible, UV, reflection and IR spectra and molar conductivities, it was concluded that the ammoniapropionatediacetate acts either as a terdentate or a quadridentate ligand in these complexes. Unlike the ATA complex, no complexes in which the nitrogen dose not coordinate with chromium could be prepared in the case of APDA. The values of the effective magnetic moments for these APDA complexes were nearly equal to the spin-only values of tervalent chromium. Further comparisons of the properties of the APDA complexes with those of the ATA complexes were also made.

The preparations of the Cr(III) complexes with ammoniatriacetic acid (ATA) have already been reported;[1,2] here ATA behaves toward a chromium(III) ion not only as a terdentate, but also as a quadridentate ligand. It was also found that some complexes have different coordinating structures in a crystal state and in an aqueous solution. When an additional methylene group ($-CH_2-$) is introduced into ATA, ammoniapropionicdiacetic acid (APDA) is obtained. It was expected that this will indicate how the behavior of APDA is chemically- and sterically-different from that of ATA in complex formation. Their rational formulae are as follows;



$$N\begin{cases} CH_2\cdot COOH \\ CH_2\cdot COOH \\ CH_2\cdot COOH \end{cases}$$

ATA



$$N\begin{cases} CH_2\cdot CH_2\cdot COOH \\ CH_2\cdot COOH \\ CH_2\cdot COOH \end{cases}$$

APDA

The purposes of the present study were: (1) to investigate as what ligand an APDA can behave toward a chromium(III) ion; (2) to find out whether or not different structures are observed between the APDA complexes in a crystal state and in an aqueous solution, and, at the same time, (3) to compare the properties of the APDA complexes with those of ATA.

Experimental

Preparation of Ammoniapropionicdiacetic Acid, $C_7H_{11}O_6N$. The method of preparation described here is a modification of that one which has already been reported by Schwarzenbach *et al.*[3]

Ninety grams of β-alanine were neutralized with 300 m*l* of water containing 40 g of sodium hydroxide. Besides, 190 g of monochloroacetic acid were dissolved into about 300 m*l* of water and then gradually neutralized with 170 g of sodium bicarbonate. These two neutralized reagents were then mixed and heated on a water bath. When the temperature of the mixed solution reached *ca.* 70°C, 200 m*l* of water containing 80 g of sodium hydroxide were added. The temperature immediately increased because of the exothermic condensation reaction. After the reaction was over, the resultant solution was cooled to room temperature. The gradual addition of concentrated hydrochloric acid and stirring with glass rod produced white, powdered crystals. The recrystallization was achieved by dissolving the crude products into water containing an appropriate amount of sodium bicarbonate, and then by gradually adding hydrochloric acid to the solution.

Yield, about 160 g.

Found: N, 6.42; C, 40.72; H, 5.39%. Calcd for $C_7H_{11}O_6N$: N, 6.84; C, 40.98; H, 5.40%.

Preparation of the Complexes. *1*) *Hydroxohydrogenammoniapropionicdiacetatodiaquochromium(III)*, $[Cr(OH)(apdaH)(H_2O)_2]$ (I). Thirteen grams of chromium(III) chloride hexahydrate were dissolved into 200 m*l* of water, and then 10 g of APDA were added to them. The mixed solution was heated on a water bath until no residue of the unreacted APDA could be seen. Then

---

*1 Presented in part at the 17th Symposium on Coordination Compounds, Hiroshima, December, 1967.

1) A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **40**, 2317 (1967).

2) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **40**, 2322 (1967).

3) G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, *Helv. Chim. Acta,* **32**, 1175 (1949).

the reddish purple crystals could easily be obtained from its cooled (room temperature) solution. The products were recrystallized from its concentrated purple solution of water. Yield, about 6 g.

Found: Cr, 16.76; N, 4.64; C, 27.61; H, 4.36%. Calcd for $[Cr(OH)(apdaH)(H_2O)_2]$: Cr, 16.84; N, 4.53; C, 27.24; H, 4.57%.

2) Ammonium Hydroxoammoniapropionicdiacetatoaquochromate(III) Dihydrate, $NH_4[Cr(OH)(apda)(H_2O)]\cdot 2H_2O$ (II). Ten grams of Complex I, obtained above, were dissolved into 200 m*l* of water containing 1.8 g of ammonium carbonate, and then the mixture was cooled to 0°C. Purple crystals were thus obtained. Recrystallization was achieved from its concentrated aqueous solution. Yield, about 2 g.

Found: Cr, 14.83; N, 7.96; C, 24.06; H, 5.87; H_2O,*2 9.8%. Calcd for $NH_4[Cr(OH)(apda)(H_2O)]\cdot 2H_2O$: Cr, 15.13; N, 8.15; C, 24.46; H, 5.57; H_2O, 10.48%.

3) Ammonium Bis-(ammoniapropionicdiacetato)chromate(III) Dihydrate, $(NH_4)_3[Cr(apda)_2]\cdot 2H_2O$ (III). Seven grams of APDA were neutralized with 200 m*l* of water containing 4 g of ammonium carbonate, and then 10 g of Complex I were added. The mixed solution was evaporated to dryness on a water bath. Crude, pale-red crystals were thus obtained. The product was recrystallized from one percent of an aqueous ammonium carbonate solution. Yield, about 2.5 g.

Found: Cr, 9.82; N, 12.90; C, 29.94; H, 6.19; H_2O, 6.8%. Calcd for $(NH_4)_3[Cr(apda)_2]\cdot 2H_2O$: Cr, 9.52; N, 12.81; C, 30.75; H, 5.89; H_2O, 6.85%.

An attempt to obtain crystals such as $NH_4[Cr(apdaH)_2]$, in which one of the carboxyl groups of an APDA does not participate in the coordination, was unsuccessful because of the deposition of the I crystals. On the other hand, in the case of ATA, we were successful in obtaining the corresponding pink crystals of $NH_4[Cr(ataH)_2]\cdot 2H_2O$.1)

4) Ammoniapropionicdiacetato-2,2′-bipyridylchromium(III) Trihydrate, $[Cr(apda)(bipy)]\cdot 3H_2O$ (IV). Ten grams of I were dissolved into 300 m*l* of water containing 3 g of ammonium carbonate, and then 5 g of 2,2′-bipyridyl neutralized with 6 m*l* of concentrated hydrochloric acid were added. After the mixed solution had been heated on a water bath until it changed from purple to reddish purple, it was cooled to 0°C. Then, brown crystals were separated out. The product was recrystallized from a concentrated aqueous solution or from alcohol. Yield, about 6 g.

Found: Cr, 10.76; N, 9.13; C, 44.49; H, 4.82; H_2O, 12.1%. Calcd for $[Cr(apda)(bipy)]\cdot 3H_2O$: Cr, 11.18; N, 9.04; C, 43.93; H, 4.63; H_2O, 11.72%.

5) Ammoniapropionicdiacetato-o-phenanthrolinechromium(III) Trihydrate, $[Cr(apda)(o\text{-}phen)]\cdot 3H_2O$ (V). Ten grams of I were dissolved into 300 m*l* of water containing 3 g of ammonium carbonate, and then 6 g of *o*-phenanthroline neutralized with 6 m*l* of concentrated hydrochloric acid were added. After the mixed solution had been heated on a water bath until it changed from purple to brown, it was cooled to 0°C; then, brown crystals were separated out. Recrystallization was achieved from water or from an alcohol solution. Yield, about 8 g.

Found: Cr, 10.16; N, 8.82; C, 46.70; H, 4.82; H_2O, 11.7%. Calcd for $[Cr(apda)(o\text{-}phen)]\cdot 3H_2O$: Cr, 10.63; N, 8.59; C, 46.68; H, 4.53; H_2O, 11.14%.

6) Ammoniapropionicdiacetatodipyridinechromium(III), $[Cr(apda)(py)_2]$ (VI). Eleven grams of Complex II were dissolved into 30 m*l* of water containing 3 m*l* of concentrated hydrochloric acid, and then 150 m*l* (excess) of pyridine were added. This solution was heated on a water bath by using a reflux-condenser. After the solution had gradually changed in color from purple to pale red, it was immediately cooled to 0°C. Pink crystals were thus obtained. The product was recrystallized from absolute alcohol or from absolute pyridine. Yield, about 3 g.

As will be mentioned below, it was found that these crystals lost the coordinated pyridine, even at room temperature.

Found: Cr, 13.15; N, 9.38%. Calcd for $[Cr(apda)(py)_2]$: Cr, 12.61; N, 10.19%.

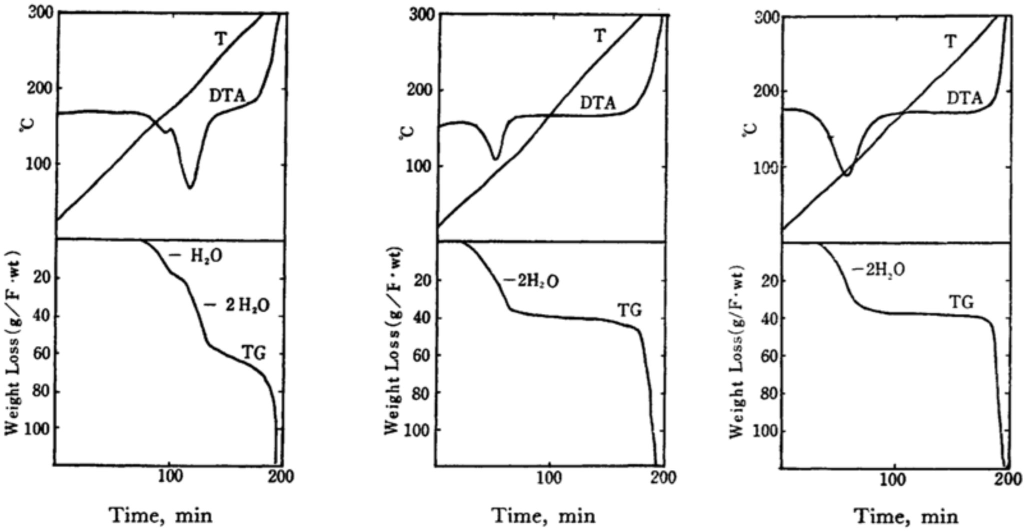
Apparatus. The UV and IR absorption spectra were measured with a Hitachi EPS Spectrometer and a Nippon Bunko IR-E Spectrometer respectively, while the reflection spectra were measured in a finely-powder solid state using a Hitachi EPU-2A Spectrometer equipped with the standard Hitachi reflection attachment. The thermal analyses and the conductivity and the magnetic-susceptibility measurement were carried out with a Metrimpex Derivatograph, a Yokogawa Universal Bridge BV-Z-13A, and a Gouy-Balance respectively.

Results and Discussion

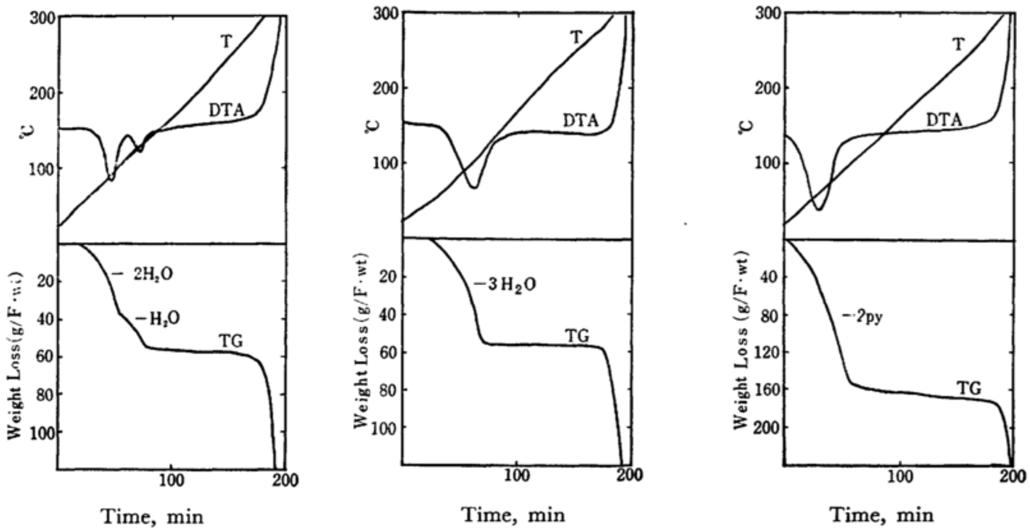
Thermal Analyses. By using the derivatograph, three measurements, a thermogravimetric analysis (TGA), a differential thermogravimetric analysis (DTG), and a differential thermal analysis (DTA), can be carried out simultaneously. In this study, above all DTA and TGA were effectively used in order to ascertain the compositions of the complexes obtained. Their DTA, TGA, and temperature curves (T) are shown in Figs. 1-(A)—(F). All the measurements were carried out at a heating rate of 1°C/min in a constant nitrogen stream. The reddish-purple crystals of I gradually lose one mole of water from 130 to 160°C, and then 2 mol of water up to 230°C, as is shown in Fig. 1(A). It was found that the color changed from reddish purple to purple and then to green during the heating. These dehydration temperatures seem to be a little higher than that of crystalline water. More detailed discussions will be undertaken elsewhere.

The waters of crystallization in Complexes II, III, and V are all evolved by the decomposition up to 130°C (Figs. 1-(B), 1-(C) and 1-(E)). For Complex IV, the initial two moles of the crystalline waters and the last one were step-by-step liberated at 90°C and 150°C respectively (Fig. 1-(D)). The coordinated pyridine molecules in VI were liberated at rather a lower temperature (from room temperature to 80°C), as is shown in Fig. 1-(F).

[*2] The H_2O appearing in all the analytical data in this paper shows the crystalline water estimated from the derivatogram.



(A) $[Cr(OH)(apdaH)(H_2O)_2]$ (B) $NH_4[Cr(OH)(apda)(H_2O)]\cdot 2H_2O$ (C) $(NH_4)_3[Cr(apda)_2]\cdot 2H_2O$



(D) $[Cr(apda)(bipy)]\cdot 3H_2O$ (E) $[Cr(apda)(o\text{-}phen)]\cdot 3H_2O$ (F) $[Cr(apda)(py)_2]$

Fig. 1. Curves for thermal analyses.

TABLE 1. BEHAVIOR TOWARD THE ION EXCHANGER AND MOLAR CONDUCTIVITIES

Complex	Color of crystal	Color of solution	Adsorption to the ion exchanger		Molar conductivities (mho cm^{-1})
			Na-form	Cl-form	
I	Reddish purple	Purple	−	−	—
II	Purple	Purple	−	+	121.2
III	Pink	Pink	−	+	346.2
IV	Brown	Brown	−	−	—
V	Brown	Brown	−	−	—
VI	Pink	Pink	−	−	—

TABLE 2. ABSORPTION MAXIMA

Complex	$\nu_1(10^{13}/\text{sec})$ $(\log \varepsilon_1)$	$\nu_2(10^{13}/\text{sec})$ $(\log \varepsilon_2)$	$\nu_3(10^{13}/\text{sec})$ $(\log \varepsilon_3)$
I	55.5 (2.03)	75.0 (1.93)	
II	53.5 (1.96)	73.5 (1.96)	
III	60.9 (1.87)	82.9 (1.61)	
IV	56.0 (1.98)	76.5 (2.09)	97.1 (4.30)
V	55.6 (1.94)	76.9 (2.12)	99.3 (3.66)
VI	57.0 (2.13)	77.5 (1.98)	107.1 (3.25)

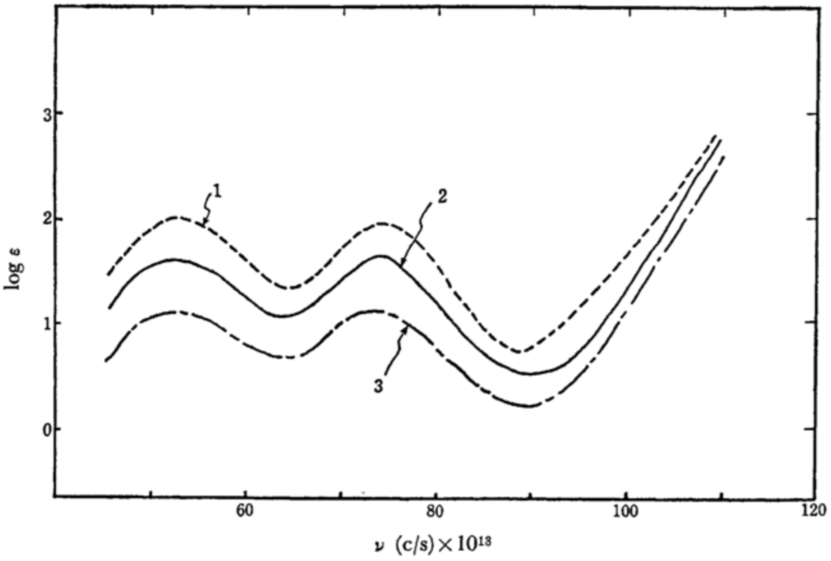


Fig. 2. Electronic absorption spectra for the solution of
1: $[Cr(OH)(apdaH)(H_2O)_2]$ 2: $[Cr(OH)(apdaH)(H_2O)_2]$ heated at 160°C
3: Purple solution of $[Cr(ata)(H_2O)_2]$.

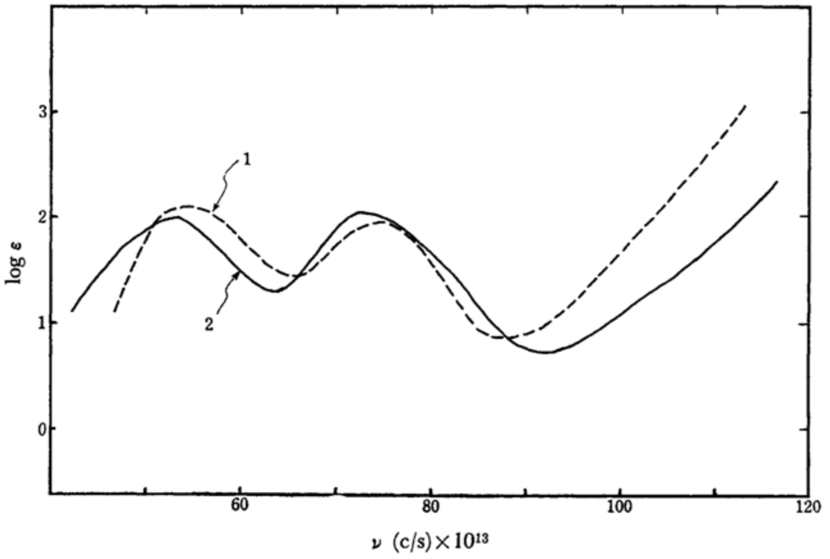


Fig. 3. Electronic absorption spectra for the solutions of
1: $NH_4[Cr(OH)(apda)(H_2O)]\cdot 2H_2O$ 2: $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$.

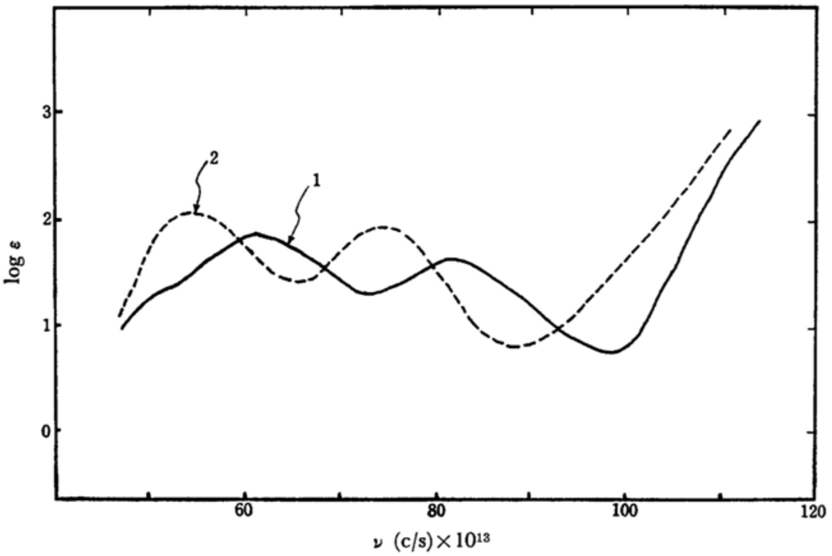


Fig. 4. Electronic absorption spectra for the solutions of
1: $(NH_4)_3[Cr(apda)_2]\cdot 2H_2O$ 2: $(NH_4)_3[Cr(apda)_2]\cdot 2H_2O$ stood overnight.

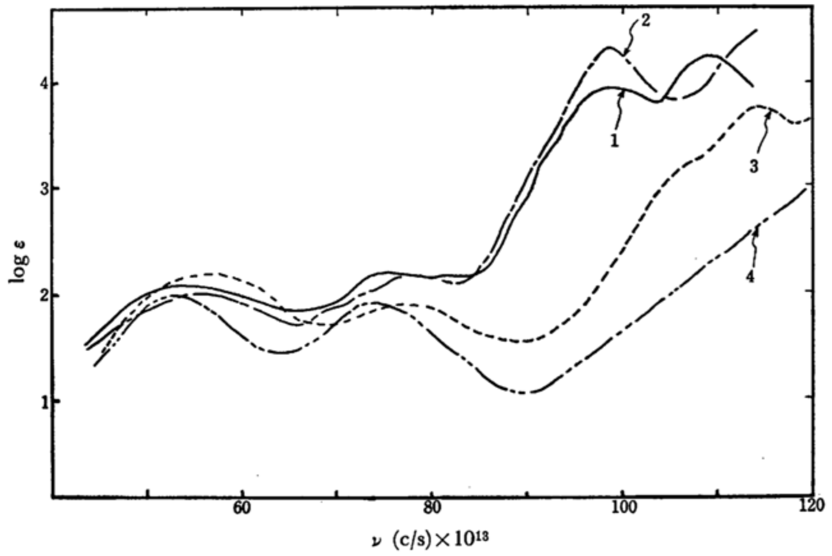


Fig. 5. Electronic absorption spectra for the solutions of
1: [Cr(apda)(*o*-phen)]$\cdot 3H_2O$ 2: [Cr(apda)(bipy)]$\cdot 3H_2O$
3: $[Cr(apda)(py)_2]$ 4: $[Cr(apda)(py)_2]$ exposed in air.

Behavior of the Complexes in Reaction to the Ion Exchanger and Their Molar Conductivity. The behavior of the complexes in reaction to the ion exchanger and the values of their molar conductivities in a 1×10^{-3} mol/*l* solution are listed in Table 1. The + sign shows the possibility of the adsorption of the complexes by the exchanger, while − shows non-adsorption. It is shown in the table that Complexes I, IV, V, and VI were not adsorbed by either exchanger, and that their molar conductivities are extremely small (1—2 mho cm^{-1}), indicating that these complexes are non-electrolytes. On the other hand, the purple crystal, II, and the pink crystal, III, are shown to be adsorbed by the anion exchanger; additionally, their molar conductivities are 121.2 and 346.2 mho cm^{-1} respectively, showing that they are 1 : 1-type and 1 : 3-type electrolytes respectively.

Electronic Absorption Spectra. The absorption spectra for the six complexes from I through VI were all measured in aqueous solutions; those for III and VI were measured in a buffer solution of pH 6 and in an alcohol-water solution, respectively in order to prevent gradual decomposition. Their spectra concerned are shown in Figs. 2—5, while the numerical values of their absorption maxima are summarized in Table 2.

Figure 2 shows the absorption spectra for the purple solutions of Complex I, of I heated at 160°C, and of the ATA complex (known to have the same structure as, [Cr(ata)(H_2O)$_2$]); in this figure the scale of the ordinate for the [Cr(ata)(H_2O)$_2$] is arbitrary. Since the spectra of these three complexes show very similar forms, they are considered to have an identical structure in solutions.

The absorption spectra of I, II, and VI for the solid state, as measured by the diffuse-reflection method, are shown in Figs. 6—8. In Fig. 6, a full line shows the absorption spectrum for the solid state of I, while a dotted line gives that of a product which has lost one mole of water upon being heated at 160°C, as has been shown in thermal analyses described above. As Figs. 2 and 6 show, the spectra for the solution of I heated at 160°C and for the solution of I itself have analogous aspects, and differ from that for the solid state of I. Therefore, it may be considered that in solution Complex I has a structure identical with that of [Cr(ata)(H_2O)$_2$], but not in a crystal state, and that certain changes in the structure occur upon heating.

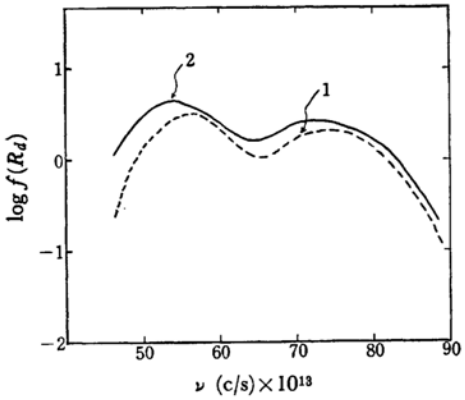


Fig. 6. Electronic absorption spectra for the solid states of
1: [Cr(OH)(apdaH)(H_2O)$_2$,
2: [Cr(OH)(apdaH)(H_2O)$_2$] heated at 160°C.

$$f(R_d) = \frac{(1-R_d)^2}{2R_d}$$

(R_d: relative reflection index)

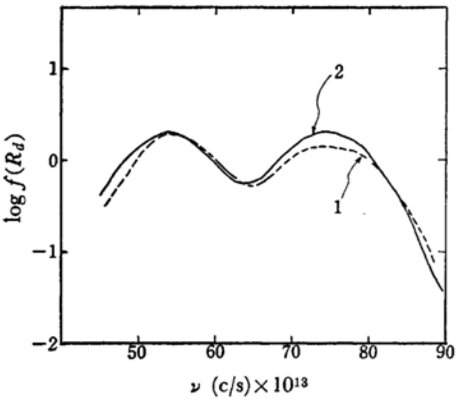


Fig. 7. Electronic absorption spectra for the solid states of
1: NH_4[Cr(OH)(apda)(H_2O)]·$2H_2O$,
2: NH_4[Cr(OH)(ata)(H_2O)]·$2H_2O$.

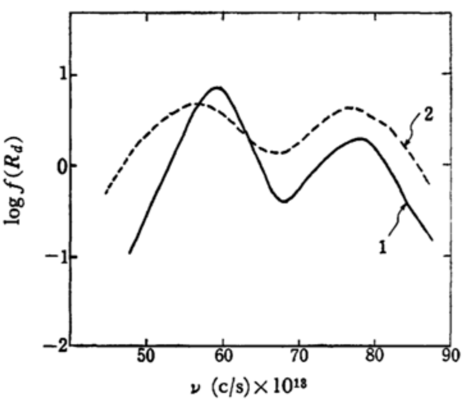


Fig. 8. Electronic absorption spectra for the solid states of
1: [Cr(apda)(py)$_2$],
2: [Cr(apda)(py)$_2$] exposed in air.

In Fig. 3, the absorption spectra of the purple crystals of II and the corresponding ATA complex are shown. These curves seem to be somewhat different from each other. On the other hand, Fig. 7 shows the absorption spectra of these complexes in the solid state; these spectra are quite similar to each other. One possible interpretation in these results is given below. In the preceding paper,$^{1)}$ as ATA complexes corresponding to II, NH_4[Cr(OH)(ata)(H_2O)]·$2H_2O$ and NH_4-[Cr(OH)(ata)(H_2O)$_2$]·$3H_2O$ were obtained. The former complex turned from purple to green when dissolved in water; from this it was concluded that this purple crystal is a [Cr·N·O_5]-type complex, while the product in the green solution was a [Cr·O_6]-type one, in which the nitrogen atom is not directly coordinated to chromium. In the latter ATA complex, also, the nitrogen atom in ATA was not directly coordinated to chromium in either a solution and in a solid state. Nevertheless, in the crystal of APDA complex II, the nitrogen atom in APDA participates in coordination together with the three carboxyl groups, and we have not succeeded in preparing the [Cr·O_6]-type complex corresponding to the green ATA complex described above.

The absorption spectra for the solutions of the pink crystal of III and of the one which was left

TABLE 3. IR DATA (cm^{-1})

Complex	-COOH	-COO-Cr	-COO-	Complement
APDA	1725(vs)			
I	1693(s)	1670(sh)—1598(vs)		
II		1670(sh)—1596(vs)		
III		1680(sh)—1595(vs)	1605(sh)	
IV		1682(sh)—1590(vs)		1588(s), 860(s), 734(s)*
V		1675(sh)—1596(vs)		1590(s), 858(s), 724(s)**
VI		1688(sh)—1590(vs)		1585(s), 753(s), 713(s)***

* The absorptions arising from 2,2′-bipyridyl.
** Those from *o*-phenanthroline.
*** Those from pyridine.

to stand overnight are shown in Fig. 4. The former spectrum indicates a splitting on the first band (a d–d electron transition). This may mean that this crystal has a *trans* structure with respect to the nitrogen atoms in APDAs. Upon standing overnight this solution gradually turned from pink to purple and its spectrum became quite similar to that of II (Figs. 3 and 4). This suggests that there is a gradual decomposition of $[Cr(apda)_2]^{3-}$ to $[Cr(OH)(apda)(H_2O)]^-$. On the other hand, $[Cr(ata)_2]^{3-}$ decomposed to $[Cr(OH)(ata)(H_2O)_2]^-$.¹⁾

Figure 5 shows the spectra for the solutions of the IV, V, and VI complexes, and that of III exposed to air for three days. The former two give complicated curves similar to those of the corresponding ATA complexes; this was a result of the coordination of 2,2′-bipyridyl and *o*-phenanthroline.²⁾ In solution, the pink crystals of VI have two absorption peaks, at 57.0 and 77.5, and a shoulder at 107.1×10^{13} c/s (in Curve 3), but the shoulder disappeared and the two peaks shifted to a longer wavelength region in VI which had been exposed to air (in Curve 4), as is shown in Fig. 5. Such a change was also found in the solid state (Fig. 8). These facts indicate that the coordinated pyridines are liberated from the crystals even at room temperature.

Infrared Spectra. The infrared spectra were measured in order to determine whether or not the carboxyl groups in the complexes were coordinated. The numerical values of the absorption bands arising from the carboxyl groups and the other ligands are listed in Table 3, while the spectra of Complex I concerning carboxyl-group stretching are shown in Fig. 9. The crystal of I gives two strong bands due to the carboxyl groups; one is a 1693 cm^{-1}, and the other is a 1670—1598 cm^{-1}. The former may be assigned to the stretching of free carboxylic acid, which disappears upon heating at 160°C, whereas the latter may be assigned to that of the coordinated carboxyl group. The shoulder at 1605 cm^{-1}, appearing only in III, suggests that it has free carboxylate ions. The other complexes show strong absorption bands in the region of 1590—1680 cm^{-1}, suggesting that all the carboxyl groups are coordinated. Further, IV, V and VI show bands reflecting the vibrations of C=C, C=N, and C–H in coordinated 2,2′-bipyridyl, *o*-phenanthroline and pyridine.

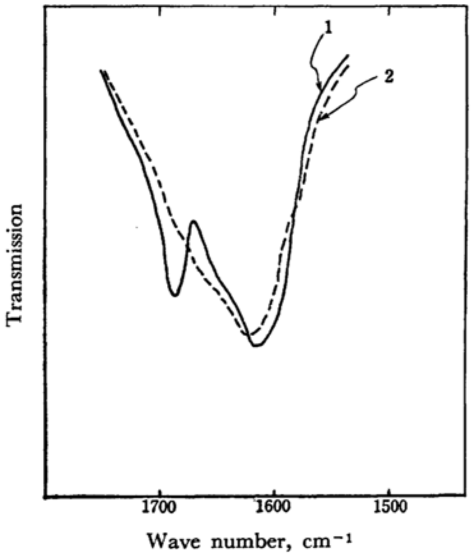


Fig. 9. Infrared spectra for
1: $[Cr(OH)(apdaH)(H_2O)_2]$,
2: $[Cr(OH)(apdaH)(H_2O)_2]$ heated at 160°C.

Magnetic Moment. The effective magnetic moments of these complexes were evaluated from the magnetic susceptibilities as measured by the Gouy method. The numerical data, corrected by introducing each Pascal constant, are summarized

TABLE 4. MAGNETIC MOMENTS (B. M.)

Complex	B. M. (temp.)
I	3.88 (293°K)
II	3.70 (293°K)
III	3.75 (293°K)
IV	3.88 (293°K)
V	3.84 (293°K)
VI	3.82 (293°K)

in Table 4. These values, 3.7—3.9 B. M., are nearly equal to the spin-only values for tervalent chromium.

Discussion of the Structures and Some Comparisons with the ATA Complexes. The possible structues of these complexes will now be discussed and comparisons will be made with the ATA complexes on the basis of the above results. Fig. 10 shows the patterns of the possible structures, (A), (B), (C), and (D), proposed by the present authors. The classification of the success or failure in the preparation of the ATA and APDA complexes of these four types are summarrized below:

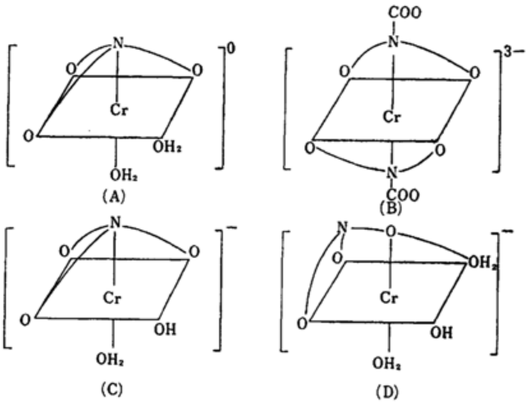
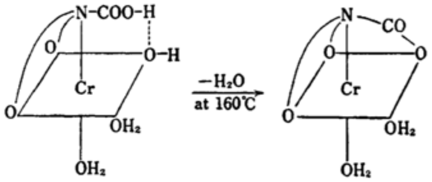


Fig. 10. Possible structures.

Type	Ligand: ATA	Ligand: APDA
A	×	○
B	○	○
C	○	○
D	○	×

where ○ indicates success in preparation and × shows failure. The crystal of the A-type complex was obtained with APDA, but not with ATA. This may be mainly due to the much lower solubility in the former complex than that in the latter. The B-type complex was prepared with both chelating agents. In the ATA complex, there was a successive decomposition from B to D, but one from B to C was found in the APDA complex. Although the C-type complex was obtained with both ligands, an instantaneous change (in an aqueous solution) into D occurred in the ATA complex, but not in the APDA complex. As has already been reported, the introduction of the methylene group ($-CH_2-$) into ATA probably results in a little more stable complex formation. The inspection by using the molecular model suggests that there is a larger strain on the nitrogen atom in coordination in the ATA complex than in that with the APDA complex. As a result of this steric factor, the nitrogen atom in APDA has the larger coordinating ability than that in ATA. This fact is consistent with the expectation as to the stability shown by Martell *et al.*[4] The failure to prepare the D-type complex, in which the nitrogen atom in APDA does not participate in the coordination, may also support such a steric reason as that described above. With all the mixed ligand complexes, the APDA always acts as a quadridentate ligand.

Finally, as is drawn below, in Complex I there are some interactions between the hydrogen atom in the free carboxylic acid and the oxygen atom in the coordinated OH group; when heated at 160°C the oxygen atom within the free carboxylic acid may participate in the coordination by losing one mole of water. A fact similar to this has previously been reported by one of the present authors.[5]



---

[4] S. Chaberek, Jr. and A. E. Martell, *J. Am. Chem. Soc.*, **75**, 2888 (1953).

[5] E. Kyuno, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure. Chem. Sect.)*, **80**, 849 (1959).