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

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A new chelating agent—ammoniaisopropionicdiacetic acid (abbreviated as AIPDA), one of the derivatives of ammoniatriacetic acid, was prepared. Also, the following chromium(III) complexes containing AIPDA as a ligand were newly prepared: $NH_4[Cr(OH)(aipda)(H_2O)]\cdot 4H_2O$ (purple) (I), $NH_4[Cr(OH)(aipda)(H_2O)_2]\cdot 2H_2O$ (green) (II), $[Cr(aipda)(o\text{-phen})]\cdot 2H_2O$ (brown) (III), $[Cr(aipda)(bipy)]\cdot 3H_2O$ (brown) (IV), [Cr(aipda)(*l*-pn)] (pink) (V), $[Cr(aipda)(py)_2]$ (pink) (VI) and $NH_4[Cr(OH)(aipda)(py)]\cdot 2H_2O$ (reddish purple) (VII), where apipda, *o*-phen, bipy, *l*-pn and py are the abbreviations of the ammoniaisopropionatediacetate ion, *o*-phenanthroline, 2,2′-bipyridyl, *l*-propylenediamine and pyridine respectively. On the basis of the chemical and thermal analyses and the measurements of the electronic absorption spectra, the reflection spectra, and the IR spectra, it was found that, in these complexes, AIPDA can behave as a terdentate or a quadridentate ligand to chromium(III), but the 1 : 2 Cr(III) AIPDA complex like the corresponding ATA one could not be obtained because of the steric hindrance resulting from the introduction of a methyl group into ATA. Further information on the conductivities in an aqueous solution and the reflection spectra suggests that V and VI are gradually aquated. The properties of the AIPDA complexes obtained in the present study were compared with those of ammoniatriacetic acid and those of ammoniapropionicdiacetic acid complexes.

The preparations of the chromium(III) complexes containing ammoniatriacetic acid (ATA) and ammoniapropionicdiacetic acid (APDA) as the chelating agents have already been reported[1-3]; these two complexes behave quite differently. For example, ATA formed a more stable complex as a terdentate (O_3 type) than as a quadridentate ($N\text{-}O_3$ type) ligand in an aqueous solution, while in the solid state it formed a more stable one as a quadridentate ligand. On the other hand, AIPDA did not behave thus as a terdentate ligand (O_3 type).

When one of the hydrogen atoms in a $-CH_2-$ group in ATA is replaced with a methyl group, ammoniaisopropionicdiacetic acid (AIPDA) is obtained. This reagent is expected to indicate any chemically and sterically unique behavior in the complex formation, differing from ATA or APDA. The formula of AIPDA is drawn in Fig. 1, together with those of ATA and APDA. AIPDA has one nitrogen and three oxygen atoms capable of coordinating; therefore, it can be expected to behave either as a quadridentate ligand ($N\text{-}O_3$ type) or as a terdentate ligand ($N\text{-}O_2$ type or O_3 type). On the basis of these observations, this study aimed to find how AIPDA behaves toward a chromium(III) ion and to compare the properties of the AIPDA complexes with those of the ATA and APDA complexes.

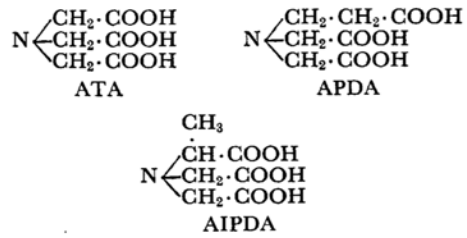

Fig. 1. Structures of the chelating agents.

Experimental

Preparation of Ammoniaisopropionicdiacetic Acid, $C_7H_{11}O_6N$. Ninety grams of *d,l*-α-alanine were neutralized with 200 m*l* of water containing 57 g of potassium hydroxide. Besides, 190 g of monochloroacetic acid was dissolved in about 300 m*l* of water and then gradually neutralized with 200 g of potassium hydrogencarbonate. The two neutralized reagents were then mixed and heated on a water bath. When the temperature of the solution was raised to *ca.* 70°C, 200 m*l* of water containing 112 g of potassium hydroxide was added. Because of the exothermic reaction, the temperature was immediately raised. After the reaction was over, an appropriate amount of concentrated hydrochloric acid was added to the solution until the

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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) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 238 (1968).

value of pH dropped from 9 to 1—2. The potassium chloride depositing out first was filtered off. The filtrate was again concentrated to as small an amount as possible. To the resultant solution, an appropriate amount of acetone was gradually added, and then the solution was scrubbed with a glass rod until white, powdered crystals were obtained, after which the solution was kept at 0°C. Recrystallization was achieved from cold water. It is considerably soluble in water, but, is insoluble in alcohol and ether. Yield, about 100 g.

Found: N, 6.43; C, 41.21; H, 5.30%. Calcd for $C_7H_{11}O_6N$: N, 6.84; C, 40.98; H, 5.40%.

Preparations of the Complexes. The methods of preparing the complexes containing AIPDA are very simmilar to those used to prepare those with ATA.[1]

1) Ammonium Hydroxoammoniaisopropionicdiacetatoaquochromate(III) Tetrahydrate, $NH_4[Cr(OH)(aipda)(H_2O)]\cdot 4H_2O$ (purple) (I). Approximately 4.2 g of AIPDA and an appropriate amount of chromium(III) hydroxide freshly prepared from 10 g of chromium alum and aqueous ammonia were mixed in 100 m*l* of hot water; then the mixture was evaporated almost to dryness. The residue was once dissolved in 30 m*l* of not water, and the resultant purple solution was filtered from the residue undissolved. By using this purple solution as a starting material, complexes I and II were prepared as below.

To this purple solution, about 1.5 g of ammonium carbonate were added and the pH was adjusted to 5—6. After it had been cooled to 0°C, purple, scale-like crystals were obtained. The products were recrystallized from their concentrated, greenish solution. Yield, about 1 g.

Found: Cr, 13.42; N, 7.26; C, 21.96; H, 6.81; H_2O,*2 19.7%. Calcd for $NH_4[Cr(OH)(aipda)(H_2O)]\cdot 4H_2O$: Cr, 13.68; N, 7.36; C, 22.12; H, 6.12; H_2O, 19.11%.

2) Ammonium Hydroxoammoniaisopropionicdiacetatodiaquochromate(III) Dihydrate, $NH_4[Cr(OH)(aipda)(H_2O)_2]\cdot 2H_2O$ (green) (II). To the purple solution obtained above, about 2.5 g of ammonium carbonate were added and the pH was adjusted to 7—8. When it was cooled to 0°C, green, scale-like crystals were obtained. Since it was, sometimes, contaminated with purple crystals of I, the pH had to be well adjusted to the above value. The recrystallization was achieved from its concentrated, greenish solution, the pH having been adjusted to 7—8 by adding an appropriate amount of ammonium carbonate. Yield, about 1 g.

Found: Cr, 14.25; N, 7.53; C, 22.96; H, 5.71; H_2O, 9.7%. Calcd for $NH_4[Cr(OH)(aipda)(H_2O)_2]\cdot 2H_2O$: Cr, 14.73; N, 7.74; C, 23.23; H, 5.85; H_2O, 10.03%.

3) Ammoniaisopropionicdiacetato - o - phenanthrolinechromium(III) Dihydrate, $[Cr(aipda)(o\text{-phen})]\cdot 2H_2O$ (brown) (III). About 6 g of *o*-phenanthroline and 2.6 m*l* of concentrated hydrochloric acid were added to about 50 m*l* of water containing 10 g of Complex I. When the solution was then heated for several minutes on a water bath, brown crystals were separated out. The recrystallization was achieved from water. Yield, about 3 g.

Found: Cr, 11.07; N, 8.90; C, 48.09; H, 4.10; H_2O, 7.5%. Calcd for $[Cr(aipda)(o\text{-phen})]\cdot 2H_2O$: Cr, 11.04; N, 8.92; C, 48.48; H, 4.28; H_2O, 7.71%.

4) Ammoniaisopropionicdiacetato-2,2'-bipyridylchlomium-(III) Trihydrate, $[Cr(aipda)(bipy)]\cdot 3H_2O$ (brown) (IV). Five grams of 2,2'-bipyridyl and 2.6 m*l* of concentrated hydrochloric acid were added to about 50 m*l* of water containing 10 g of I. When the solution was then heated on a waterbath for several minutes, brown crystals were obtained. The products were recrystallized from water. Yield, about 4 g.

Found: Cr, 11.02; N, 9.27; C, 44.00; H, 4.11; H_2O, 12.0%. Calcd for $[Cr(aipda)(bipy)]\cdot 3H_2O$: Cr, 11.18; N, 9.04; C, 43.93; H, 4.63; H_2O, 11.72%.

5) Ammoniaisopropionicdiacetato - l - propylenediaminechromium(III), $[Cr(aipda)(l\text{-pn})]$ (pink) (V). About 2 g of *l*-propylenediamine were diluted with 20 m*l* of water and then 2.4 m*l* of concentrated hydrochloric acid were added. To this solution, a 50 m*l* portion of water containing 10 g of I was added, and resultant solution was evaporated to dryness; pink powdered crystals were thus obtained. The crude products were recrystallized from an alcohol-water (1 : 1) mixture. Yield, about 2 g. In an aqueous solution, these crystals were gradually aquated.

Found: Cr, 15.61; N, 12.21; C, 36.94; H, 5.54%. Calcd for $[Cr(aipda)(l\text{-pn})]$: Cr, 15.84; N, 12.80; C, 36.58; H, 5.52%.

The use of *d*- or racemic-propylenediamine instead of *l*-propylenediamine gave a corresponding *d*- or *d,l*-pn complex.

6) Ammoniaisopropionicdiacetato - bis (pyridine) chromium-(III), $[Cr(aipda)(py)_2]$ (pink) (VI). Then grams of I were dissolved into 10 m*l* of water containing 2.4 m*l* of concentrated hydrochloric acid, and then 150 m*l* of pyridine were added to it. This mixture was heated on a water bath, using a reflux condenser in order to prevent the pyridine from vaporizing. After the solution had gradually turned from purple to pale red, it was cooled to 0°C. After it had then stood for a few days, pink crystals were obtained. The recrystallization was achieved from absolute alcohol or absolute pyridine. Yield, about 1 g.

Found: Cr, 12.91; N, 9.54%. Calcd for $[Cr(aipda)(py)_2]$: Cr, 12.61; N, 10.19%.

The elementary analyses were repeated several times, but fully satisfactory results could not be obtained since the crystals easily lose the pyridine, even at room temperature. On the basis of the derivatography, the change in the TGA curve, corresponding to two moles of pyridine, reasonably supports such a composition as $[Cr(aipda)(py)_2]$.

7) Ammonium Hydroxoammoniaisopropionicdiacetatopyridinechromate(III) Dihydrate, $NH_4[Cr(OH)(aipda)(py)]\cdot 2H_2O$ (reddish purple) (VII). Ten grams of I were dissolved into 50 m*l* of water, and then 25 m*l* of pyridine was added to the mixture. Being gradually heated on a water bath at *ca.* 40—60°C, the solution turned from green to pink. As soon as reddish purple crystals appeared, the crystals had to be quickly filtered off from the solution since the purple crystals, I, were inclined to deposit as a by-product. The recrystallization from water was always unsuccessful due to the deposition of the purple crystals, I. Moreover, since no optimum solvent for VII was found, no recrystallization could be done. Yield, about 1.5 g. For the above reasons, the results of the elementary analyses were not in

*2 The H_2O which appears in all the analytical data in this paper shows the only distinct crystalline water estimated from the derivatogram.

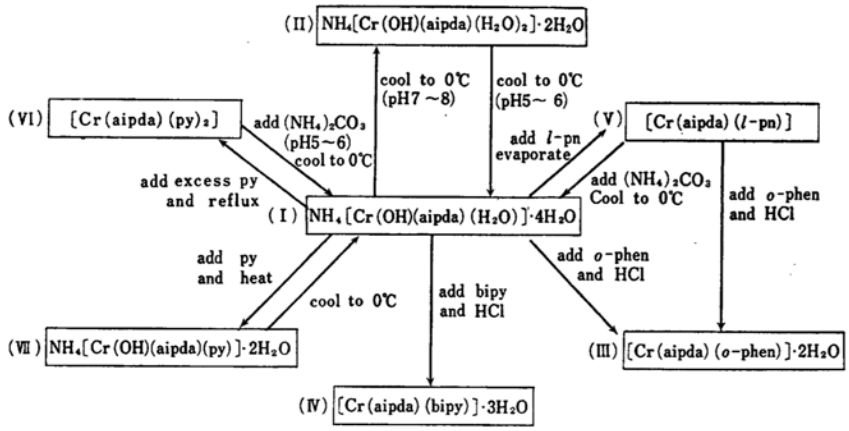


Fig. 2

excellent agreement with the calculated values shown below.

Found: Cr, 12.24; N, 9.80; C, 35.28; H, 4.97; H_2O, 8.2%. Calcd for $NH_4[Cr(OH)(aipda)(py)]\cdot 2H_2O$: Cr, 12.83; N, 10.38; C, 35.59; H, 5.45; H_2O, 8.92%.

The crystalline-water content in these complexes was estimated from the weight loss in the respective thermogravimetric curves (TGA), which were measured with a derivatograph.

Preparative Interconversion among These Complexes. Some interconversions among the complexes prepared in the present work were successful, as in the case of ATA. In Fig. 2, several interconversion procedures are shown schematically.

A) The Interconversion from I to II and Vice Versa. The pH of the greenish solution of I was adjusted to 7—8 by adding small amounts of amonium carbonate; when it had cooled to 0°C, green crystals, II, were obtained. On the other hand, when hydrochloric acid was used instead of ammonium carbonate, the pH of the greenish solution of II was descreased to 5—6 at 0°C, and purple crystals of I were obtained.

B) The Interconversion from V or VI to I. To 10 m*l* of an aqueous solution containing 1 g of V or VI, 0.2 or 0.3 g of ammonium carbonate was added respectively. These solutions turned from pink to green. When they were cooled to 0°C, purple crystals, I, were obtained.

C) The interconversion from V to III. One gram of *o*-phenanthroline was dissolved into 20 m*l* of water containing about 0.5 m*l* of concentrated hydrochloric acid. To this solution, 1.7 g of V were then dissolved by heating it on a water bath. The solution gradually changed from pink to brown. After the resultant solution had stood for several days, brown crystals, III, were obtained.

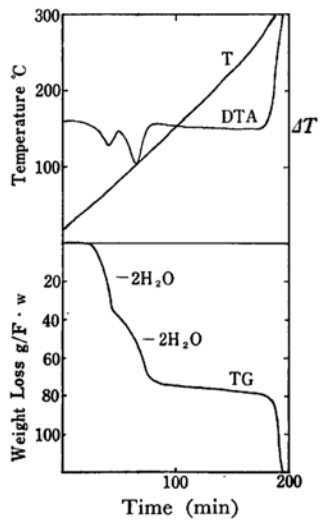
Apparatus. The apparatus used in this study was the same as has been described in a previous paper.[3)]

Results and Discussion

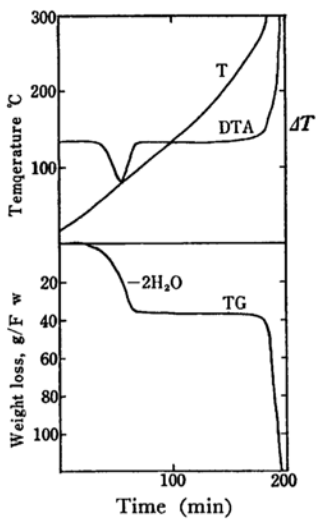
Thermal Measurements. The DTA, TGA, and temperature curves obtained for the complexes are shown in Figs. 3-A to 3-G, where the scale of DTA is arbitrary; the upper-side deviation of DTA indicacates the appearance of an exothermic reaction, and the under-side one, that of the endothermic reaction. All the measurements were carried out with a heating rate of 1°C/min in a nitrogen stream. As can be seen in Figs. 3-A to 3-D, the I, II, III, and IV complexes are all dehydrated between about 60 and 120°C and decomposed at about 290—300°C. Especially the step-by-step dehydration was observed for Complexes I and III. Figure 3-E shows that Complex V has no crystalline water. The complexes of VI and VII are shown in Figs. 3-F and 3-G to lose their coordinated pyridines, even at relatively low temperatures (from room temperature to 80°C). Moreover, in Complex VII, as may be seen in Fig. 3-G, the liberation of crystalline water was well detected after it had lost coordinated pyridine.

The values of the enthalpy changes in these decomposition processes, which can be evaluated from the DTA curves, will be reported elsewhere.

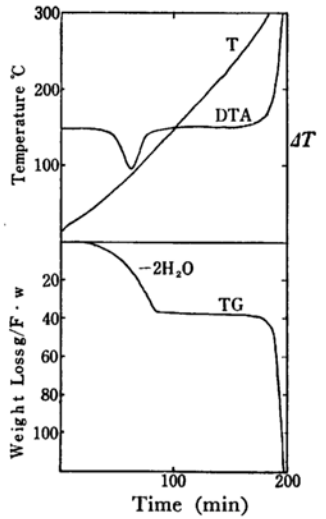
Behavior in Reaction to the Ion Exchanger and Molar Conductivity. The behavior in reaction to the ion exchangers and molar conductivities of a 1/1000 molar solution of the samples are shown in Table 1, in which the + symbol indicates the adsorption of the complexes by an exchanger, and −, the non-adsorption. The solutions of the purple crystals, I, and the green crystals, II, were both greenish and were adsorbed by the Cl-form anion exchanger. Their molar conductivities are 115.0 and 116.2 mho cm^{-1} respectively, suggesting that they are 1 : 1-type complexes. The value of the conductivity, 98.6 mho cm^{-1}, for VII and its ability to be adsorbed by the Cl-form exchanger indicate that it is also of this type. The complexes of III to VI were adsorbed neither by the Na-form nor the Cl-form exchanger, showing that they are all non-electrolyte molecules. A gradual decomposition in an aqueous solution was found for both V and VI, when their colors turned purple, and the decomposed solutions could not be adsorbed by the exchangers, suggesting that the aquations probably, in part at



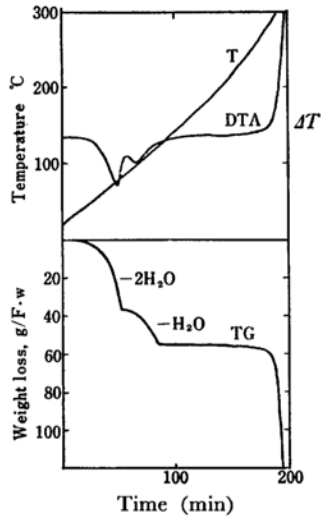
(A) $NH_4[Cr(OH)(aipda)(H_2O)]\cdot 4H_2O$



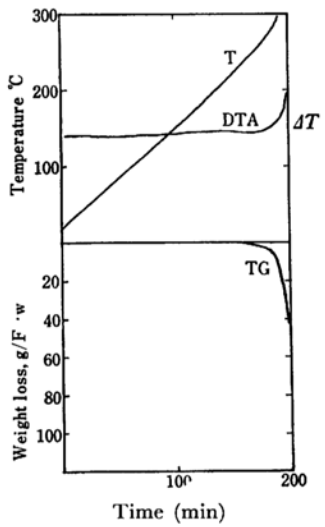
(B) $NH_4[Cr(OH)(aipda)(H_2O)_2]\cdot 2H_2O$



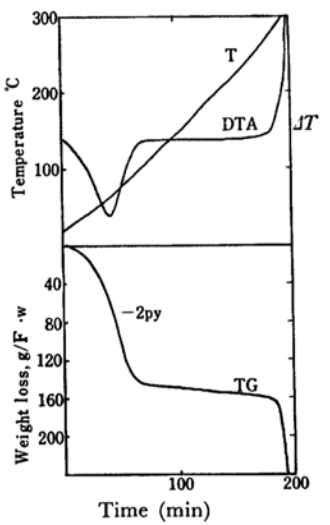
(C) $[Cr(aipda)(o\text{-phen})]\cdot 2H_2O$



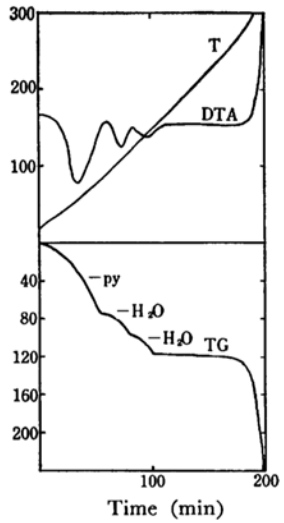
(D) $[Cr(aipda)(bipy)]\cdot 3H_2O$



(E) [Cr(aipda)(*l*-pn)]



(F) $[Cr(aipda)(py)_2]$



(G) $NH_4[Cr(OH)(aipda)(py)]\cdot 2H_2O$

Fig. 3. Curves for thermal analyses.

TABLE 1. BEHAVIOR TOWARD THE ION EXCHANGER AND MOLAR CONDUCTIVITY

Complex	Color of crystal	Color of solution	Adsorption		Molar conductivity (mho cm^{-1})
			Na-form	Cl-form	
I	purple	green	−	+	115.0
II	green	green	−	+	116.2
III	brown	brown	−	−	
IV	brown	brown	−	−	
V	pink	pink	−	−	
VI	pink	pink	−	−	
VII	reddish purple	reddish purple	−	+	98.6

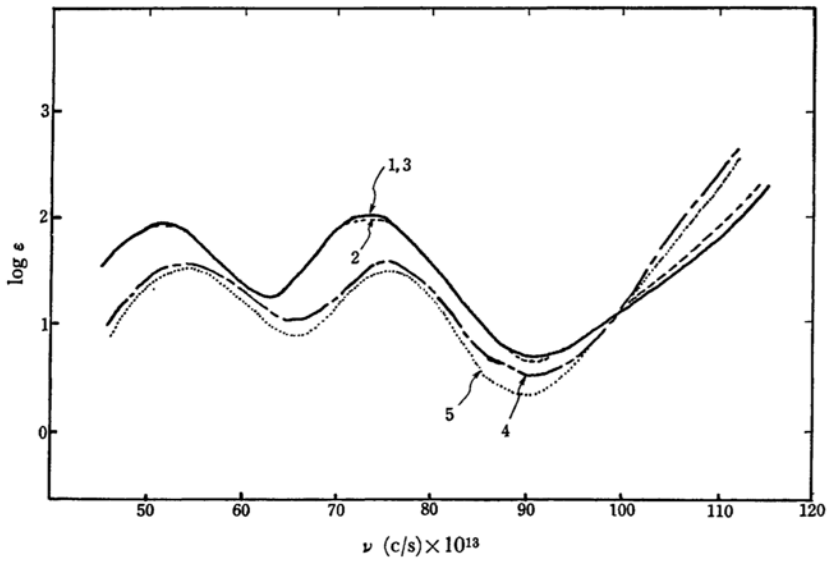


Fig. 4. Electronic absorption spectra for the solutions of
1: $NH_4[Cr(OH)(aipda)(H_2O)]\cdot 4H_2O$, 2: $NH_4[Cr(OH)(aipda)(H_2O)_2]\cdot 2H_2O$,
3: $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$, 4: $[Cr(aipda)(H_2O)_2]$, 5: $[Cr(ata)(H_2O)_2]$.

TABLE 2. ABSORPTION MAXIMA

Complex	$\nu_1(\log \varepsilon_1)$	$\nu_2(\log \varepsilon_2)$	$\nu_3(\log \varepsilon_3)$
I	51.5(1.95)	73.5(2.01)	
II	51.5(1.92)	73.5(2.00)	
III	55.9(1.91)	76.1(2.09)	99.0(3.71)
IV	56.3(1.95)	76.7(2.05)	97.1(4.18)
V	55.5(1.98)	78.5(2.04)	
VI	57.0(2.13)	77.5(1.98)	107.1(3.25)
VII	54.5(2.01)	74.3(2.08)	112.8(3.68)

least, take place.

Electronic Absorption Spectra. The Absorption spectra for Complexes I to VII were measured in an aqueous solution; of these, those for V and VI were done in a mixture of water-alcohol (1 : 1) to prevent gradual decomposition. The numerical data of the absorption maxima are summarized in Table 2. The spectra for the solutions of Complexes I and II are drawn in Fig. 4, together with

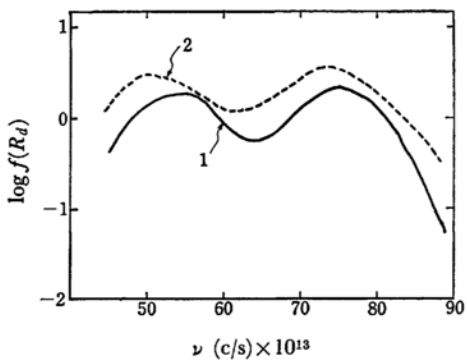


Fig. 5. Electronic absorption spectra for the solid sate of
1: $NH_4[Cr(OH)(aipda)(H_2O)]\cdot 4H_2$,
2: $NH_4[Cr(OH)(aipda)(H_2O)_2]\cdot 2H_2O$.
$f(R_d)=\dfrac{(1-R_d)^2}{2R_d}$
(R_d: relative reflection index).

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

Complex	-COOH	-COO-Cr	$-COO^-$	Complement
I		1688(sh)—1598(vs)		
II		1680(sh)—1596(vs)		
III		1681(sh)—1598(vs)		1595(s), 863(s), 731(s)*
IV		1678(sh)—1595(vs)		1590(s), 861(s), 730(s)**
V		1680(sh)—1593(vs)		
VI		1675(sh)—1598(vs)		1585(s), 753(s), 712(s)**
VII		1693(sh)—1597(vs)		1583(s), 746(s), 710(s)***

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

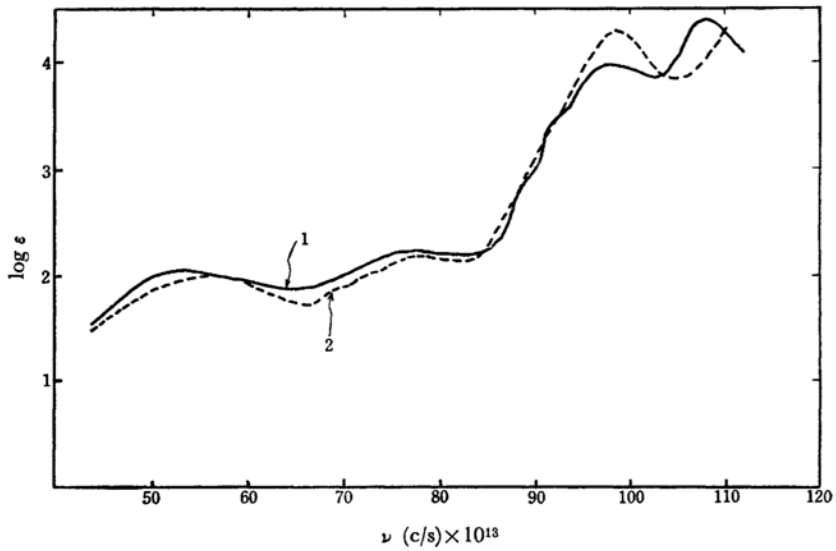


Fig. 6. Electronic absorption spectra for the solutions of
1: $[Cr(aipda)(o\text{-phen})\cdot 2H_2O$, 2: $[Cr(aipda)(bipy)]\cdot 3H_2O$.

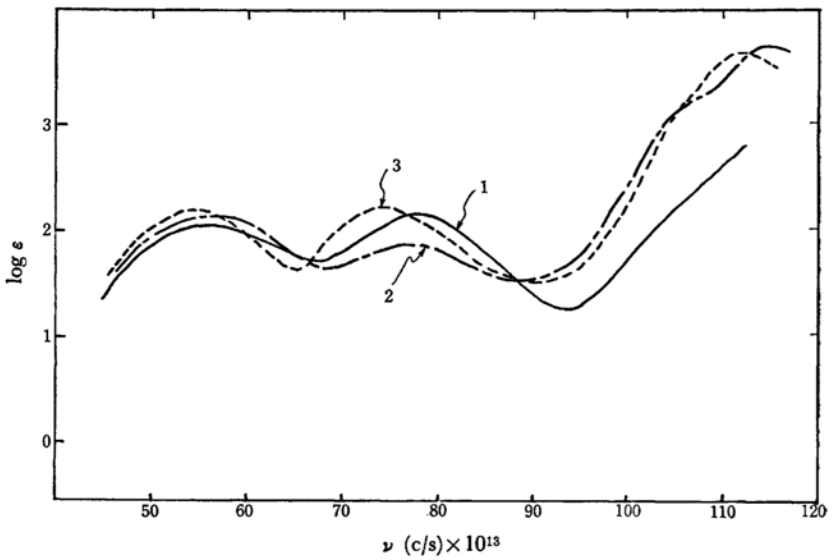


Fig. 7. Electronic absorption spectra for the solutions of
1: $[Cr(aipda)(l\text{-pn})]$, 2: $[Cr(aipda)(py)_2]$, 3: $NH_4[Cr(OH)(aipda)(py)]\cdot 2H_2O$.

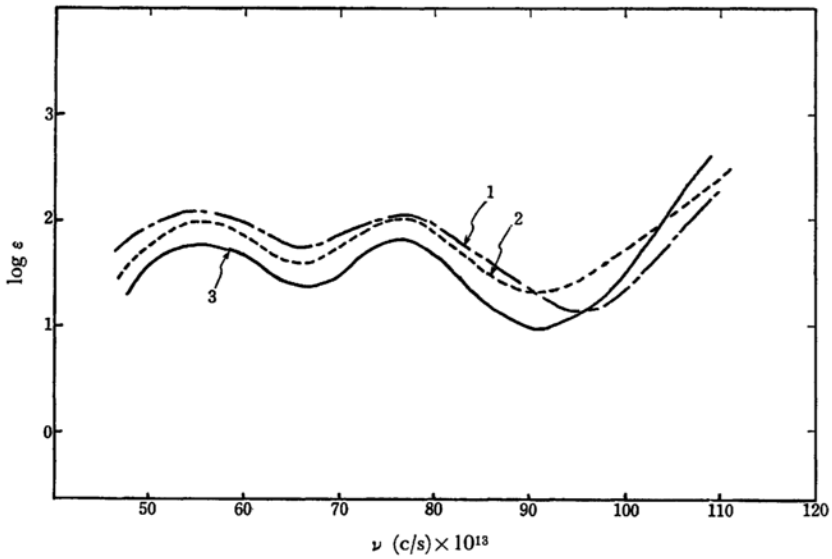


Fig. 8. Electronic absorption spectra for
1: [Cr(aipda)(*l*-pn)] stood in water, 2: [Cr(aipda)(py)$_2$] stood in water.

those for the corresponding ATA complexes and for the purple solutions of AIPDA and ATA complexes, where the scale of log ε for the purple solutions is arbitrary. A very close resemblance was seen among the spectra for the solutions of I, II, and the corresponding ATA complex.

The absorption spectra for the solid state were measured by the diffuse-reflection method. The spectra for the solid state of I and II are shown in Fig. 5. An appreciable difference between them can be seen. From these data, as with the corresponding ATA complex,[1] both the purple complex, I, and the green complex, II, may be considered to have the same structure, of the [Cr·O$_6$] type in an aqueous solution, whereas in the crystal state they have different structures (*i. e.*, the purple complex is of the [Cr·N·O$_5$] type, and the green complex, of [Cr·O$_6$] type). In addition, the purple solution used as a starting material gave a spectrum very similar to that of the corresponding purple solution of the ATA complex, showing that they have the same structure.

The spectra for the solutions of the brown crystals of III and IV gave complicated curves similar to those of the corresponding ATA and APDA complexes due to the coordination of 2,2′-bipyridyl and *o*-phenanthroline, as can be seen in Fig. 6.

The absorption spectra for the solutions of the pink crystal V, the pink crystal VI, and the reddish-purple crystal VII are drawn in Fig. 7. The complexes of VI and VII show a third absorption maximum, due to the coordinated pyridine. The complexes of V and VI in an aqueous solution have a tendency to lose *l*-propylenediamine and pyridine respectively, and their spectra are found to approach that of the purple solution used as a starting material, as is shown in Fig. 8. This indicates that these complexes may undergo aquation by losing *l*-propylenediamine and the pyridine molecule respectively. Figure 9 shows the absorption spectra for the solid states of Complex VI itself and Complex VI after it has been exposed to air for a few days. A considerable difference between them can be seen; namely, the latter has its maximum at a lower frequency region than the former. This shows that VI easily loses the coordinated pyridine molecules, even at room temperature. Such a phenomenon has also been found in the corresponding APDA complex.[3]

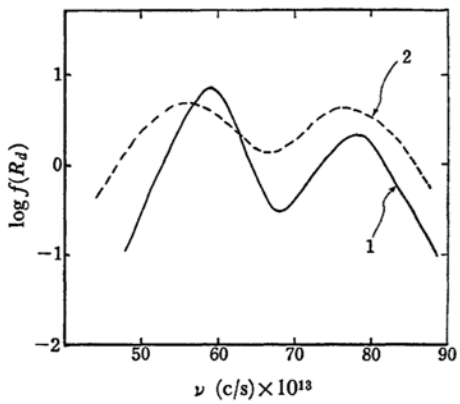


Fig. 9. Electronic absorption spectra for the solid states of
1: [Cr(aipda)(py)$_2$], 2: [Cr(aipda)(py)$_2$] exposed.

IR Spectra. The infrared spectra were measured in order to determine whether or not the carboxyl groups in the complexes are coordinating. The

numerical values of the band arising from the carboxyl groups and the other ligands concerned are listed in Table 3. Strong absorption bands in the 1589—1670 cm^{-1} region can be detected in all these complexes, indicating that all the carboxyl groups in AIPDA participate in the coordination. Furthermore, III, IV, VI, and VII gave bands connected with the vibrations of C–C, C–N, and C–H in coordinated 2,2'-bipyridyl, *o*-phenanthroline, and pyridine.

Magnetic Moments. The magnetic susceptibilities of the complexes were measured by the Gouy method. The numerical data of the effective magnetic moments, as evaluated from the above values, are listed in Table 4. The values for these complexes are 3,75—3.95 B. M., nearly equal to their spin-only values for chromium(III).

TABLE 4. MAGNETIC MOMENTS (B. M.)

Complex	μ_{eff} B. M. (temp. °K)
I	3.82 (293°K)
II	3.91 (293°K)
III	3.87 (293°K)
IV	3.85 (293°K)
V	3.87 (293°K)
VI	3.75 (293°K)
VII	3.81 (293°K)

Discussion of the Structures. *1) Possible Structures of the Complexes Obtained.* The possible structures of these complexes proposed by the present authors on the basis of the above results are given in Fig. 10. The complex species in the solution used as a starting material may have an A structure. The structure for purple crystals, I, may be identified as a C. In green crystals, II, a D structure, may hold in the same way as in the corresponding ATA complex, although the positions of the OH^- and H_2O ligands are still arbitrary. No complex with a B structure was found. In all the mixed-ligand complexes, only AIPDA acted as a quadridentate ligand.

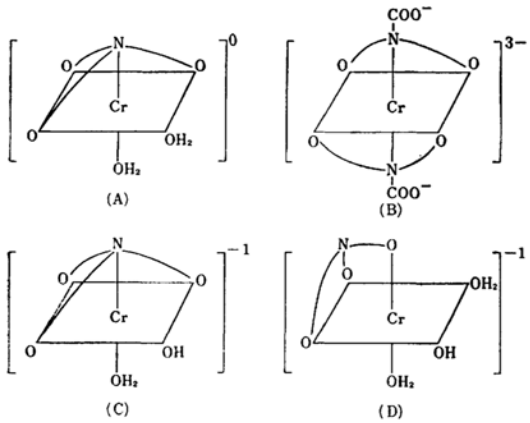


Fig. 10. Possible structures.

2) Some Comparisons among ATA, AIPDA, and APDA Complexes. Of these three ligands, ATA and AIPDA behave toward the chromium(III) ion quite similar manners, but that of APDA is somewhat different. The classification of success or failure in preparing the complexes as a crystal state are summarized in Table 5, where ○ symbolizies a successful preparation and × shows failure. It is immediately noticeable that an A-type complex can be prepared only with APDA; this may be mainly due to the lesser solubility of the complex in water. Their solubilities decrease in the order: AIPDA>ATA>APDA complexes.

TABLE 5. THE COMPLEXES OBTAINED AS A CRYSTAL STATE

	ATA	AIPDA	APDA
A type	×	×	○
B type	○	×	○
C type	○	○	○
D type	○	○	×

○, symbolizes the successful preparation.
×, the reverse.

All these ligands can form C-type complexes. Furthermore, the C-type complexes with ATA and AIPDA were changed instantly to the D-type when dissolved into water, whereas the corresponding C-type complex with APDA did not act thus. These facts may be briefly explained as follows. ATA and AIPDA form three five-membered chelate rings in the complex formation, while APDA forms two five-membered rings and one six-membered one. The inspection by using a molecular model suggests that there are larger strains on the nitrogen atom in coordinated ATA and AIPDA than that in APDA. As a result of these steric factors, the nitrogen atom in APDA has a larger coordinating ability than those in ATA and AIPDA. This fact is consistent with the expectation regarding the stability of Martell *et al.*[4] The attempt to prepare the B-type complex was not successful with AIPDA. This may be because steric hindrance due to the methyl group may arise on the formation of the 1 : 2-type complex; this possibility is supported by an inspection of the molecular model.

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