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The Chromium(III) Complexes with β -Aminoethylsulfonic-*N,N*-diacetic Acid and Aspartic-*N,N*-diacetic Acid^{*1}

Akira UEHARA, Eishin KYUNO and Ryōkichi TSUCHIYA

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

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The following chromium(III) complexes with the β -aminoethylsulfonic-*N,N*-diacetic acid (AEDA) and aspartic-*N,N*-diacetic acid (ASDA) were newly prepared; $K_3[Cr(aeda)_2] \cdot 4H_2O$ (pale red) (I), $[Cr(OH)(Haeda)(o\text{-phen})] \cdot 2H_2O$ (orange) (II) and $[Cr(Hasda)(H_2O)_2] \cdot H_2O$ (reddish purple) (III). From the results of spectral measurements, it was found that AEDA acts as a quadridentate ligand as well as a terdentate one in an aqueous solution, but only as a terdentate ligand in a crystal state, and that the coordinating ability of the oxygen atom of sulfonic radical in AEDA is weaker than that of carboxylic radical in ammoniopropionidiacetic acid (APDA). In Complex III, ASDA behaved as a quadridentate ligand rather than as a quinquedentate. Complexes II and III showed some interesting thermal decomposition processes. The former lost one mole of water at 110°C from the hydrogen atom in free sulfonic acid radical and the coordinated OH group, accompanied with the increase of coordination number of AEDA from 3 to 4. In the latter, one mole of crystalline water was lost first, and then the carboxylic acid bound to the methylene group at β -position in the ligand was decomposed to liberate carbon dioxide, and the coordinated asda was changed into apda.

Preparations and properties of chromium(III) complexes with ammoniatricacetic acid (ATA),¹⁾ ammoniopropionidiacetic acid (APDA) and ammoniaisopropionidiacetic acid (AIPDA)²⁾ have already been reported. These ligands have one nitrogen and three oxygen atoms capable of coordinating. Thus their maximum coordination number is commonly four. But it has often been pointed out that their coordinating behaviors are somewhat different from each other because of the

differences in their structures and in their chemical properties such as acid dissociation constants.^{1,2)}

Although the complexes of (A) and (B) types in Fig. 1, which shows the possible structures of complexes, were obtained in an aqueous solution with all three ligands, the crystals of (A) type were obtained only with APDA. One reason for this may be due to the small solubility of APDA complex. The (B) type complex containing ATA or AIPDA instantly changed to (C) type when they were dissolved in water, but the (C) type complex could not be obtained in the case of APDA. This sug-

^{*1} Presented in part at the 18th Symposium on Coordination Compounds, Kyoto, October (1968).

1) A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **40**, 2317, 2322 (1967).

2) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 2385, 2393 (1968).

gests that the complex containing 5-, 5- and 6-membered chelate rings with ligand such as APDA is more stable than that having three five-membered rings with ligand such as ATA or AIPDA. The complex assigned to (D) type could not be obtained only with AIPDA. This suggests that some steric hindrance due to a methyl group exists in the case of AIPDA.²⁾

β -Aminoethylsulfonic-*N,N*-diacetic acid and aspartic-*N,N*-diacetic acid (abbreviated as AEDA and ASDA, respectively) were selected as the related ligand to ATA, APDA and AIPDA in the present work. Rational formulas of these ligands are shown in Fig. 2.

This study was undertaken (1) to investigate how AEDA and ASDA behave toward metal in these complexes, (2) to prepare various complexes containing these ligands and (3) to compare the complexing properties of AEDA and ASDA with those of ATA, APDA or AIPDA.

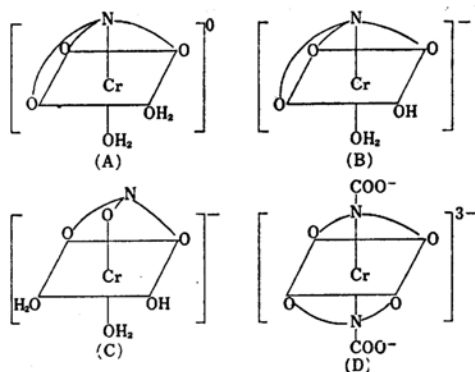


Fig. 1. Structures of the complexes.

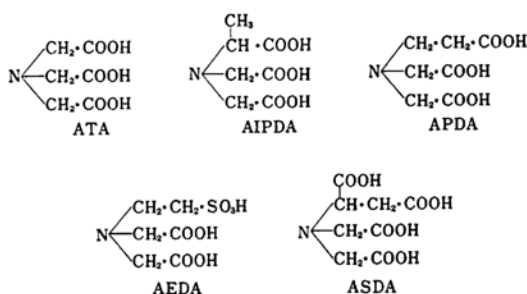


Fig. 2. Rational formulas of the ligands.

Experimental

Preparation of Ligands. β -Aminoethylsulfonic-*N,N*-diacetic Acid Dihydrate: $C_6H_{11}O_7NS \cdot 2H_2O$. The method described here is the modified one reported by Schwarzenbach *et al.*³⁾ Twenty five grams of taurine were neutralized with 100 ml of water containing about 8 g of sodium hydroxide. Thirty-nine grams of mono-

chloroacetic acid were dissolved in 200 ml of water and 34 g of sodium bicarbonate was gradually added to it. The two solutions were mixed, the mixture was heated on a water bath up to about 70°C, and 16 g of sodium hydroxide in 50 ml of water was added. Heating was continued about one hour. After cooling, gradual addition of concentrated hydrochloric acid and scrubbing by a glass rod, produced white powdered crystals. Recrystallization was achieved from water. Yield about 15 g.

Found: N, 4.96; C, 25.78; H, 5.38%. Calcd for $C_6H_{11}O_7NS \cdot 2H_2O$: N, 5.05; C, 25.99; H, 5.45%.

Aspartic-*N,N*-diacetic Acid: $C_6H_{11}O_8N$. Twenty six grams of aspartic acid were suspended in about 200 ml of water, and 35 g of sodium bicarbonate was added little by little under magnetic stirring. Thirty eight grams of monochloroacetic acid were neutralized with about 200 ml of water containing 35 g of sodium bicarbonate. After the two solutions were mixed, the mixture was heated on a water bath at 70–80°C, and then 50 ml of water containing 15 g of sodium hydroxide was added. Heating was continued for 1 hr in order to complete the reaction. After cooling, the solution was made acidic with concentrated hydrochloric acid, and then evaporated to a half volume. The sodium chloride was filtered off whenever it was separated out. After the filtrate was concentrated up to syrupy state, a small amount of acetone was added, and the solution was kept for several days in a refrigerator. White powdered crystals were obtained. The crude products were recrystallized from an acetone-water (1 : 1) mixture. Yield about 3 g.

Found: N, 5.49; C, 38.22; H, 4.37%. Calcd for $C_6H_{11}O_8N$: N, 5.62; C, 38.56; H, 4.44%.

Preparation of Complexes. *Potassium Bis(β -aminoethylsulfonic-*N,N*-diacetato)chromate (III) Tetrahydrate:* $K_2[Cr(aceda)_2] \cdot 4H_2O$ (I). Two and a half grams of chromium chloride hexahydrate were dissolved in 200 ml of water and then 2.5 g of AEDA was added. The mixture was heated on a water bath. The color of the solution changed from green to purple as the reaction proceeded. Two and a half grams of AEDA and 3 g of potassium bicarbonate were added and the solution was heated. When the color of the solution became red, the pH was adjusted to *ca.* 6. The pale red crystals were obtained from the cooled solution. The crude products were recrystallized from water. Yield about 1 g. The use of ammonium carbonate instead of potassium bicarbonate gave the ammonium salt.

Found: N, 3.81; C, 20.06; H, 3.25%. Calcd for $K_2[Cr(aceda)_2] \cdot 4H_2O$: N, 3.90; C, 20.07; H, 3.37%.

Hydroxohydrogen- β -aminoethylsulfonic-*N,N*-diacetato-*o*-phenanthrolinechromium(III) Dihydrate: $[Cr(OH)(Haeda)(o-phen)] \cdot 2H_2O$ (II). The procedure was the same as mentioned above until the purple solution was obtained. To the resulting solution, 2 g of *o*-phenanthroline was added. The pH of the solution was adjusted to 4–5 by adding an appropriate amount of potassium bicarbonate. Orange crystals were obtained from the cooled resulting solution. Recrystallization was achieved from an aqueous solution. Yield about 1.5 g.

Found: N, 8.32; C, 41.25; H, 4.14%. Calcd for $[Cr(OH)(Haeda)(o-phen)] \cdot 2H_2O$: N, 8.01; C, 41.22; H, 4.23%.

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

Hydrogenaspartic-N,N-diacetatochromium(III) Monohydrate: $[\text{Cr}(\text{Hasda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (III). The mixture of five grams of ASDA and an appropriate amount of chromium hydroxide was suspended in water, and was heated on a water bath almost to dryness. The residue was dissolved in a small amount of water, and the reddish purple filtrate was concentrated. The resulting solution was adjusted to pH 2, and after adding a small amount of acetone, it was kept in a refrigerator for a few days. Reddish purple crystals were obtained. Recrystallization was carried out from water-acetone (70 : 30) mixture. Yield about 0.5 g.

Found: N, 3.81; C, 27.59; H, 3.83%. Calcd for $[\text{Cr}(\text{Hasda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$: N, 3.97; C, 27.28; H, 3.99%

Instruments. The instruments used in this work were the same as described previously.²⁾

Results and Discussion

Observation on Thermal Decomposition Processes by using a Derivatograph and an IR Spectrometer. Some interesting thermal decomposition processes were observed by using a derivatograph and an IR spectrometer. Their derivatograms measured in a nitrogen stream with a heating rate of *ca.* 1°C/min are shown in Fig. 3. About 500 mg of the sample was used for each run. Figures 4 and 5 give the IR spectra of these complexes and of the samples taken out at several heating steps.

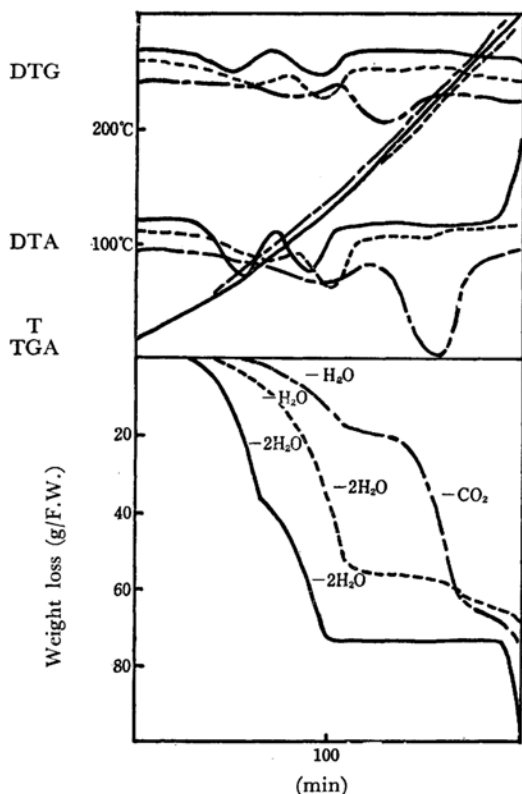


Fig. 3. Derivatograms for I (—), II (---) and III (-.-.).

As shown in Fig. 3, Complex I lost 4 mol of crystalline water in two distinct steps: the first two moles were removed at *ca.* 80°C and the last two, at 135°C. A violent decomposition started at *ca.* 280°C.

For Complex II, though TGA curve shows the weight loss corresponding to 3 mol of water from 65 to 150°C, both DTA and DTG curves indicate the split peaks below and over *ca.* 110°C. The corresponding difference could also be detected in IR spectra, which is shown in Fig. 4. The split bands at *ca.* 1200 cm^{-1} probably assigned to sulfonate ion changed to one peak when the complex was heated at 110°C, and the band due to H_2O (3400—3200 cm^{-1}) disappeared at 150°C. These facts combined with the TGA curve mean that the weight loss at the first step until 110°C is due to the evolution of one mole of water from the hydrogen ion of free sulfonic acid and the hydroxyl group and that at the second step over 110°C corresponds to the liberation of two moles of the crystalline water.

From Complex III, the weight loss corresponding to the liberation of one mole of water and to that of one mole of carbon dioxide can be observed at 75—155°C and 180—250°C on TGA curve in Fig. 3, respectively. As shown in IR spectral features in Fig. 5, both the bands at 1730 and at 1610 cm^{-1} could be detected in the sample before heating; the former has been assigned to non- and the latter, to coordinated carboxylic acid.⁴⁾

The sample at 155°C shows the same pattern, but the band at 1730 cm^{-1} disappears at 250°C. Nevertheless, the band at 3500 cm^{-1} due to the OH stretching vibration can be seen in all these samples. The results suggest that the crystalline water is lost first, and then the free carboxylic acid attached to the methylene group at β -position in the ligand is decomposed to produce carbon dioxide without losing any coordinated water, and the coordinated asda is changed into apda.

Visible and UV Absorption Spectra. All the measurements of absorption spectra were carried out in aqueous solutions. In Fig. 6, the spectrum of Complex I and that of the corresponding ATA complex are shown. The spectra of the purple solution obtained by the reaction of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with AEDA and of the solution of $[\text{Cr}(\text{ata})(\text{H}_2\text{O})_2]$ are shown in the figure. Figure 7 gives the spectra of Complex II and Complex III. The numerical data of their absorption maxima are summarized in Table 1, together with those measured in Complex III by a diffuse-reflectance method. As seen in Fig. 6, the spectrum of Complex I is quite similar to that of the corresponding ATA complex, indicating that they may have the analogous structure. Although it is known that the gradual

4) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

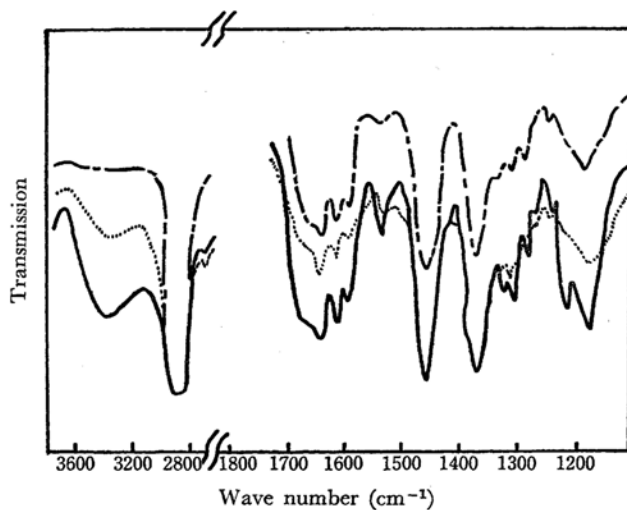


Fig. 4. Infrared spectra for II. (room temp.: —, 110°C: ---, 150°C: ···)

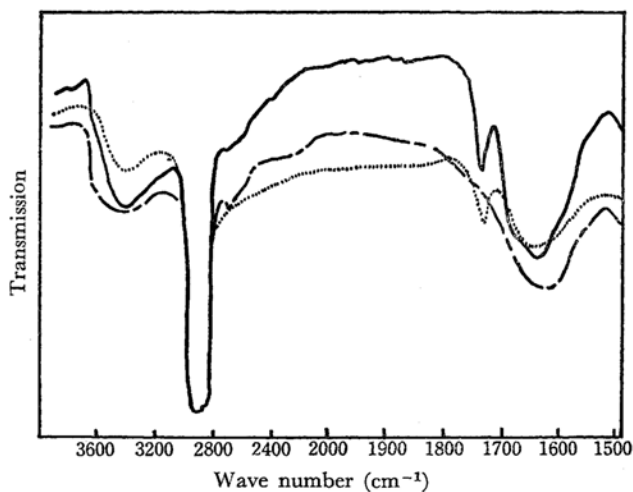


Fig. 5. Infrared spectra for III. (room temp.: —, 155°C: ---, 250°C: ···)

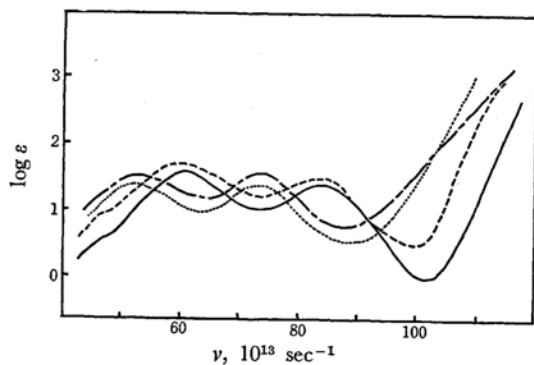


Fig. 6. Electronic Spectra for I (—), K₃[Cr(ata)₂]·4H₂O (---), [Cr(ata)(H₂O)₂] (— · —) and purple solution produced by the reaction of CrCl₃·6H₂O with AEDA (····).

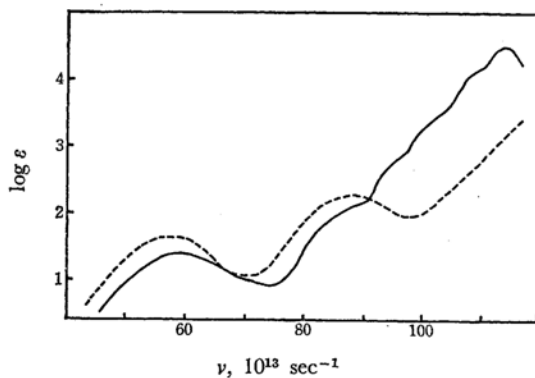


Fig. 7. Electronic spectra for II (—) and III (---).

TABLE 1. ABSORPTION MAXIMA

Complex	$\nu_1(10^{13}/\text{sec})$ (log ϵ_1)	$\nu_2(10^{13}/\text{sec})$ (log ϵ_2)
Purple solution of [Cr(aeda)(H ₂ O) ₂]	54.1 (1.89)	74.4 (2.01)
Purple solution of [Cr(ata)(H ₂ O) ₂]	54.9 (1.91)	74.1 (2.03)
I	60.0 (1.54)	83.3 (1.39)
K ₃ [Cr(ata) ₂]·4H ₂ O ¹⁾	60.1 (1.65)	83.6 (1.48)
II	59.0 (1.51)	88.2 (2.02)
III	58.4 (1.64)	86.9 (2.25)
III*	54.5	75.0

* This absorption maximum was measured by a diffuse-reflectance method.

decomposition from [Cr(ata)₂]³⁻ to [Cr(OH)(ata)(H₂O)₂]⁻ proceeds in an aqueous solution even at room temperature,¹⁾ no change in the spectrum could be observed even in the solution kept for a few days in the case of Complex I.

The spectrum for the purple solution of AEDA is very similar to that of [Cr(ata)(H₂O)₂], showing that they may have an analogous structure, and that AEDA acts as a quadridentate ligand in an aqueous solution only in this complex.

As shown in Fig. 7, Complex II gives a rather complicated spectrum due to the coordinated *o*-phenanthroline. The spectrum of Complex III in an aqueous solution has the maxima at 58.4 and 86.9 × 10¹³/sec, whereas that in a solid state measured by a diffuse-reflectance method shows the maxima at 54.5 and 75.0 × 10¹³/sec. This considerable deviation may indicate that Complex III has a different structure in an aqueous solution and in a solid state. The numerical data given in Table 1 show that the bands in a solid state of Complex III are very close to that of [Cr(ata)(H₂O)₂]. In other words, Complex III will have a coordinating structure similar to that of [Cr(ata)(H₂O)₂] in a solid state. In an aqueous solution, however, the coordinating structure is still unknown.

Molar Conductivities and pH Values. In Table 2, the values of molar conductivities and pH were listed together with the behaviors toward ion exchangers. The sign + means the adsorption of the complex by ion exchangers, and -, the reverse. All three complexes in solution were adsorbed by Cl-form anion exchangers. For Complex I, the pH value and molar conductivity were 6.8 and 383.1 mho cm⁻¹, respectively, showing that it is a 1 : 3 type electrolyte.

The solution of Complex II was acidic (pH 3.4) and molar conductivity was 161.3 mho cm⁻¹. It suggests that the hydrogen ion is partly dissociated from Haeda in an aqueous solution.

For Complex III, the values of considerably low pH (pH 1.8) and of the higher conductivity (481.2 mho cm⁻¹) were observed, which may indicate that the strong dissociation of hydrogen ion in free carboxylic acid takes place in an aqueous solution.

TABLE 2. SOME PROPERTIES OF THE COMPLEXES

Complex	Adsorption to the ion exchanger		Molar conductivity* (mho cm ⁻¹)	pH**
	Na-form	Cl-form		
I	-	+	383.1	6.8
II	-	+	161.3	3.4
III	-	+	481.2	1.8

* 1.0 × 10⁻³ mol/l aqueous solution was used.

** 1.0 × 10⁻² mol/l aqueous solution was used.

Possible Structures of the Complexes.

From the results, the possible structures proposed are depicted in Fig. 8. The purple solution formed from the reaction of chromium chloride hexahydrate with AEDA may have (a) type structure, in which AEDA acts as a quadridentate ligand. For Complex I, (b) type may be assigned, where the sulfonic acid is not coordinated. The (c) type structure having some interaction between the hydrogen atom in the sulfonic acid and the oxygen atom in the coordinated hydroxyl group seems to be reasonable for Complex II.

When ASDA acts as a quadridentate ligand, two kinds of characteristic coordinating structures are expected. One makes three five-membered chelate rings, and the other two five- and one six-membered chelate rings. However, as it has already been reported,^{2,5)} the latter case makes a more stable complex formation than the former, so that the preferable structure for Complex III is the (d) type.

Comparisons among AEDA-, ATA-, AIPDA-, and APDA-Complexes. As the structure of AEDA resembles that of APDA, it was expected that AEDA forms a stable complex in which AEDA acts as a quadridentate ligand. However, this was proved not to be the case by the following results. Firstly, the complex in which AEDA acts as a quadridentate ligand was formed in an aqueous

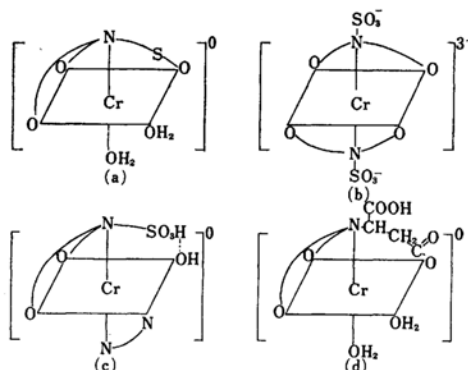


Fig. 8. Possible structures.

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

solution, but not in a crystal state. Secondly, in the mixed complexes, ATA, AIPDA and APDA behaved only as a quadridentate ligand, whereas AEDA acts as a terdentate ligand owing to the non-coordination of the sulfonic acid. Thirdly, although the ATA and APDA complexes gradually decomposed in an aqueous solution from $[\text{Cr}(\text{ata})_2]^{3-}$ and $[\text{Cr}(\text{apda})_2]^{3-}$ to $[\text{Cr}(\text{OH})(\text{ata})(\text{H}_2\text{O})_2]^-$ and $[\text{Cr}(\text{OH})(\text{apda})(\text{H}_2\text{O})]^-$ respectively, the coordinating AEDA complex I underwent no change in an aqueous solution. These facts suggest that the coordinating ability of the oxygen atom of sulfonic acid in AEDA is smaller than that of carboxylic acid in APDA. They are in good agreement with the result that APDA has larger stability constants than AEDA in the bivalent metal complexes.⁶⁾

Possible Thermal Decomposition Processes.

The possible thermal decomposition processes for Complexes II and III are described schematically in Fig. 9. Complex II lost one mole of water at 110°C from the hydrogen atom in free sulfonic acid and the coordinated hydroxyl group, resulting in the increase of coordination number of AEDA from 3 to 4. Such phenomena have also been observed in APDA complex, $[\text{Cr}(\text{OH})(\text{Hapda})(\text{H}_2\text{O})_2]^{2-}$.²⁾ On the other hand, for Complex III, one mole of crystalline water is first lost and then

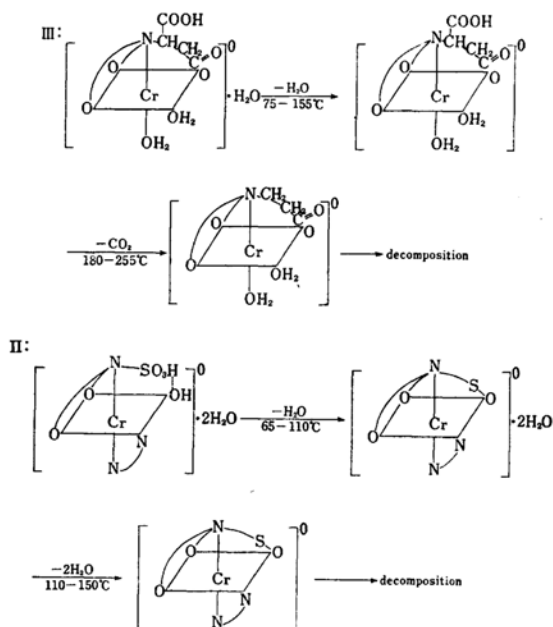


Fig. 9. Possible thermal decomposition schemes for II and III.

the carboxylic acid attached to the carbon atom at β -position in the ligand may be decomposed into carbon dioxide, and the coordinated asda is changed into apda.

6) H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 1543 (1949).