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Cobalt(III) Complexes with Nitrilotriacetic Acid, Nitrilopropionicdiacetic Acid and Nitriloisopropionicdiacetic Acid*[1]

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The following cobalt(III) complexes containing nitrilotriacetic acid (NTA), nitrolopropionicdiacetic acid (NPDA) and nitriloisopropionicdiacetic acid (NIPDA) were prepared: $(NH_4)_3[Co(nta)_2]\cdot 2H_2O$ (pink) (I), $NH_4[Co(Hnta)_2]\cdot 2H_2O$ (pale pink) (II), $K_3[Co(npda)_2]\cdot 2H_2O$ (pink) (III), $K[Co(Hnpda)_2]\cdot 3H_2O$ (pale pink) (IV), [Co(npda)(*o*-phen)]$\cdot H_2O$ (reddish violet) (V), [Co(npda)(bipy)] (reddish violet) (VI), $K[Co(OH)(nipda)(H_2O)]\cdot H_2O$ (bluish violet) (VII) and [Co(nipda)(*o*-phen)] (reddish violet) (VIII); where nta, npda, nipda, *o*-phen and bipy are the abbreviations of nitrilotriacetate-, nitrilopropionicdiacetate-, nitriloisopropionicdiacetate-ion, *o*-phenanthroline and 2,2′-bipyridyl, respectively. On the basis of electronic spectra, it was found that complexes I to IV have the *trans* form, while complexes V, VI and VIII have the *mer* form structure with respect to the nitrogen atoms in the coordinating ligands. Complex VII showed a dehydration-dimerization reaction on heating by "Derivatograph". Comparison of chemical and physical properties of the complexes with those of the corresponding chromium(III) complexes was made.

All the chelating agents discussed in this paper, NTA, NPDA and NIPDA,*[2] can behave as ($N-O_3$), ($N-O_2$) or (O_3) type ligands toward metals. Some behaviors of NTA in cobalt(III)[1] and chromium(III) complexes[2] have been reported. Several

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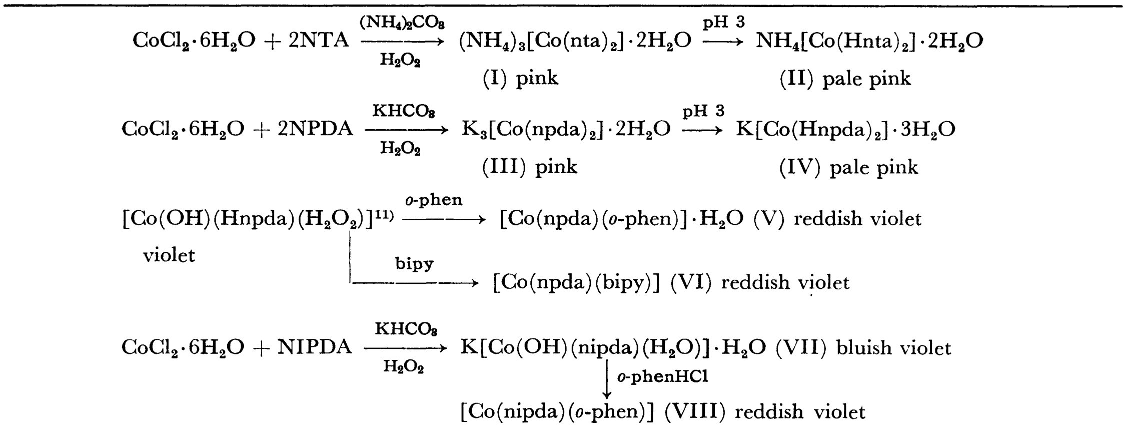
*[2] The abbreviations used in this paper, NTA, NPDA and NIPDA, correspond to ATA in Ref. 2, APDA in Ref. 11 and AIPDA in Ref. 12 respectively.

[1] M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, **31**, 940 (1958).

[2] A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **40**, 2317 (1967).

TABLE 1. PREPARATIVE SCHEMES OF COMPLEXES



$$CoCl_2\cdot6H_2O + 2NTA \xrightarrow[H_2O_2]{(NH_4)_2CO_3} \underset{\text{(I) pink}}{(NH_4)_3[Co(nta)_2]\cdot2H_2O} \xrightarrow{\text{pH 3}} \underset{\text{(II) pale pink}}{NH_4[Co(Hnta)_2]\cdot2H_2O}$$

$$CoCl_2\cdot6H_2O + 2NPDA \xrightarrow[H_2O_2]{KHCO_3} \underset{\text{(III) pink}}{K_3[Co(npda)_2]\cdot2H_2O} \xrightarrow{\text{pH 3}} \underset{\text{(IV) pale pink}}{K[Co(Hnpda)_2]\cdot3H_2O}$$

$$\underset{\text{violet}}{[Co(OH)(Hnpda)(H_2O_2)]^{11)}} \xrightarrow{o\text{-phen}} [Co(npda)(o\text{-phen})]\cdot H_2O \text{ (V) reddish violet}$$

$$[Co(OH)(Hnpda)(H_2O_2)] \xrightarrow{\text{bipy}} [Co(npda)(bipy)] \text{ (VI) reddish violet}$$

$$CoCl_2\cdot6H_2O + NIPDA \xrightarrow[H_2O_2]{KHCO_3} K[Co(OH)(nipda)(H_2O)]\cdot H_2O \text{ (VII) bluish violet} \xrightarrow{o\text{-phenHCl}} [Co(nipda)(o\text{-phen})] \text{ (VIII) reddish violet}$$

mixed complexes of cobalt(III) with NTA and with natural amino acids have been prepared and discussed in relation to the structural isomers.[3] The bis type complexes of cobalt(III)[4-7] and chromium(III)[8,9] with aminodicarboxylic acids have been reported by many workers, and speculations for their geometrical isomers have also been made. The chromium(III) complexes with aminotricarboxylic acids such as NTA or NPDA have been reported by the authors,[10-12] who pointed out that the coordinating behaviors of these agents toward chromium appreciably vary with each other due to the difference of their structures and properties. However, no report has been given about the corresponding cobalt(III) complexes.

In this study we have undertaken to (1) prepare various kinds of the cobalt(III) complexes with these ligands, (2) ascertain the coordinating behaviors of these ligands toward cobalt(III), (3) predict their structures, especially those of bis type complexes, and (4) compare the structures of the cobalt(III) complexes with those of the corresponding chromium(III) complexes.

Experimental

Preparation of Ligands. NTA,[2] NPDA,[11] and NIPDA[12] were prepared by the methods given in literature.

Preparation of Complexes. The preparative methods of the complexes are schematically shown in Table 1.

Ammonium Bis-(nitrilotriacetato)cobaltate(III) Dihydrate, $(NH_4)_3[Co(nta)_2]\cdot2H_2O$ (pink) (I). 100 m*l* of water containing 38 g of NTA was gradually neutralized with 17 g of ammonium carbonate. To this solution, 100 m*l* of aqueous solution containing 24 g of cobalt(II) chloride hexahydrate was added. After the pH of the mixed solution was adjusted to 6—7 by means of ammonium carbonate, 10 m*l* of 28% hydrogen peroxide solution was added in order to oxidize the cobalt(II) solution. On being heated on a water bath, the solution turned to pink from violet. The pink crude crystals were obtained from the resulting solution evaporated almost to dryness. The crude products were recrystallized from 5% ammonium carbonate solution. Yield about 8 g.

Found: N, 13.53; C, 27.30; H, 5.21%. Calcd for $(NH_4)_3[Co(nta)_2]\cdot2H_2O$: N, 13.32; C, 27.41; H, 5.34%.

Ammnoium Bis-(hydrogennitrilotriacetato)cobaltate(III) Dihydrate, $NH_4[Co(Hnta)_2]\cdot2H_2O$ (pale pink) (II). Five grams of complex I was dissolved in about 50 m*l* of water. When the pH of the solution was adjusted to 3 by adding a few drops of hydrochloric acid, pale pink crystals came out easily. Recrystallization was achieved from an aqueous solution. Yield about 3 g.

Found: N, 8.58; C, 27.78; H, 4.62%. Calcd for $NH_4[Co(Hnta)_2]\cdot2H_2O$: N, 8.55; C, 27.31; H, 4.48%.

Potassium Bis-(nitrilopropionicdiacetato)cobaltate(III) Dihydrate, $K_3[Co(npda)_2]\cdot2H_2O$ (pink) (III). These crystals were prepared by a procedure analogous to that in complex I except for the use of 40 g of NPDA and 9 g of potassium hydrogen carbonate instead of 38 g of NTA and 17 g of ammonium carbonate. Yield 6 g.

Found: N, 4.73; C, 27.89; H, 3.13%. Calcd for $K_3[Co(npda)_2]\cdot2H_2O$: N, 4.54; C, 27.25; H, 3.24%.

Potassium Bis-(hydrogennitrilopropionicdiacetato)cobaltate(III) Trihydrate, $K[Co(Hnpda)_2]\cdot3H_2O$ (pale pink)

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[3] N. Koine, N. Sakota, J. Hidaka and Y. Shimura, This Bulletin, **42**, 1583 (1969).

[4] M. Mori, M. Shibata, E. Kyuno and F. Maruyama, *ibid.*, **35**, 75 (1962).

[5] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

[6] D. W. Cooke, *ibid.*, **5**, 1141 (1966).

[7] J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **35**, 567 (1962).

[8] K. Yamasaki and S. Ito, *Proc. Japan Acad.*, **42**, 1077 (1966).

[9] J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

[10] A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **40**, 2322 (1967).

[11] A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 2385 (1968).

[12] A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 2393 (1968).

(IV). These crystals were also prepared by a procedure similar to that in complex II except that complex III was used instead of complex I as the starting material.

Found: N, 5.11; C, 29.96; H, 4.60%. Calcd for $K[Co(Hnpda)_2]\cdot 3H_2O$: N, 5.00; C, 30.11; H, 4.30%.

Nitrilopropionicdiacetato-o-phenanthrolinecobalt(III) Monohydrate, $[Co(npda)(o\text{-phen})]\cdot H_2O$ (reddish violet) (V). Two grams of hydroxonitrilopropionicdiacetatodiaquocobalt(III)[13] was dissolved in 100 m*l* of water and 1 g of *o*-phenanthroline was then added. On heating the color of the solution gradually turned to reddish violet from violet. From the resulting solution which was kept in a refrigerator, reddish violet crystals were obtained. Recrystallization was achieved from water. Yield 1 g.

Found: N, 9.37; C, 49.58; H, 4.02%. Calcd for $[Co(npda)(o\text{-phen})]\cdot H_2O$: N, 9.15; C, 49.69; H, 3.95%.

Nitrilopropionicdiacetato-2,2′-bipyridylcobalt(III), [Co(npda)(bipy)] (reddish violet) (VI). The preparative method is similar to that described in the case of complex V except that 1 g of 2,2′-bipyridyl was used in place of *o*-phenanthroline. Yield 1 g.

Found: N, 10.01; C, 47.16; H, 3.82%. Calcd for [Co(npda)(bipy)]: N, 10.07; C, 47.93; H, 3.86%.

Potassium hydroxonitriloisopropionicdiacetatoaquocobaltate(III) Monohydrate, $K[Co(OH)(nipda)(H_2O)]\cdot H_2O$ (bluish violet) (VII). 200 m*l* of water containing 20 g of NIPDA was neutralized with 24 g of potassium hydrogen carbonate. To the solution, 24 g of $CoCl_2\cdot 6H_2O$ was added. After the pH of the solution was adjusted to 6—7 by the addition of potassium hydrogen carbonate, 10 m*l* of 28% hydrogen peroxide solution was added in order to oxidize cobalt(II) solution. From the resulting solution kept at room temperature for a few days, bluish violet crystals were obtained. They were recrystallized from water. Yield 8 g.

Found: N, 3.74; C, 24.02; H, 3.92%. Calcd for $K[Co(OH)(nipda)(H_2O)]\cdot H_2O$: N, 3.98; C, 23.80; H, 3.71%.

Nitriloisopropionicdiacetato-o-phenanthrolinecobalt(III) Monohydrate, $[Co(nipda)(o\text{-phen})]\cdot H_2O$ (reddish violet) (VIII). After two grams of complex VII was dissolved in 100 m*l* of hot water, 1 g of *o*-phenanthroline neutralized with hydrochloric acid was added. The color of the solution turned from violet to reddish violet. From the cooled solution, reddish violet crystals separated. Recrystallization was carried out from water. Yield 0.4 g.

Found: N, 8.58; C, 47.48; H, 4.28%. Calcd for $[Co(nipda)(o\text{-phen})]\cdot H_2O$: N, 8.80; C, 47.82; H, 4.22%.

Apparatus. The same apparatus as described previously was used.[11]

Results and Discussion

Magnetic Properties and Molar Conductivities. Magnetic susceptibilities were measured by the Gouy method in order to ascertain whether the cobalt in the complexes is tervalent or not. The results are listed in Table 2 together with the values of molar conductivities. All the complexes showed diamagnetic properties, indicating that the tervalent cobalt of low-spin type participates in coordination in these complexes.

TABLE 2. MAGNETIC PROPERTIES AND MOLAR CONDUCTIVITIES

Complexes	Magnetic Properties*	Molar Conductivities** (mho cm^{-1})
I	diamagnetic	325
II	diamagnetic	366
III	diamagnetic	333
IV	diamagnetic	372
V	diamagnetic	<10
VI	diamagnetic	<10
VII	diamagnetic	102
VIII	diamagnetic	<10

* measured at 293°K

** 10^{-3} mol/*l* of aqueous solution was used.

Molar conductivities were measured to investigate to what valency-type the complexes belong in an aqueous solution. As can be seen from Table 2, the values for complexes I and III are 325 and 333 mho cm^{-1}, showing that they are 1 : 3 valency-type electrolytes. The larger values for complexes II (366 mho cm^{-1}) and IV (372 mho cm^{-1}) than those for I and III may be due to the partial dissociation of the hydrogen ion of free carboxylic acid. The very small conductivities of V, VI and VIII suggest that they are non-electrolytes. The value 102 mho cm^{-1} for complex VII is fairly reasonable for the 1 : 1 type electrolyte.

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

Complexes	-COOH	COO-M	COO$^-$	Complements
I		1620 (vs)	1595 (sh)	
II	1753 (s)	1610 (vs)		
III		1628 (vs)	1598 (sh)	
IV	1715 (s)	1626 (vs)		
V		1655 (vs)		850, 1590*
VI		1665 (vs)		780, 1590**
VII		1650 (vs)		
VIII		1658 (vs)		865, 1595*

* The absorptions arising from *o*-phenanthlorine

** Those from 2,2′-bipyridyl

IR Spectra. The infrared absorption spectra of the complexes were measured at a nujol mull state to inspect how the carboxylic groups in the ligands behave toward metals. The numerical data of the absorption bands arising from the free carboxylic (–COOH), the coordinated carboxylic (–COO–M) and the ionic carboxylic groups (–COO$^-$) are given in Table 3 together with the values assigned to the other ligands coordinated. Assignments of the bands were also followed

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[13] R. Tsuchiya, A. Uehara and E. Kyuno, This Bulletin, **42**, 1886 (1969).

by Busch and Bailar.[14] In the spectra of all the complexes, the bands assigned to the coordinated carboxylic group are confirmed. The bands arising from the free carboxylic acid appeared in both the spectra of complexes II and IV. The spectra of complexes I and III show the bands due to the ionic carboxylic groups.

Coordinating Structures of the Complexes. From the results, the coordinating structures of the complexes are discussed.

It has been mentioned from MO treatments that in the cobalt(III) complexes of N_2–O_4 type, the *trans* form with respect to nitrogen atoms shows the splitting in the first absorption band at the longer wave length region,[15] and it has been established in the complexes such as K[Co(ox)(gly)$_2$][16] and K[Co(ida)$_2$].[7]

The numerical data of the absorption maxima of the complexes due to *d–d* transitions are summarized in Table 4.

TABLE 4. ABSORPTION MAXIMA

Complexes	ν_1(10^{13}/sec)(log ε_1)	ν_2(10^{13}/sec)(log ε_2)
I	57.58 (1.83)	81.97 (2.27)
II	57.58 (1.81)	81.74 (2.25)
III	58.71 (1.90)	82.87 (2.10)
IV	58.71 (1.91)	82.64 (2.15)
V	56.29 (2.34)	77.92 (2.34)
VI	55.76 (2.36)	77.92 (2.34)
VII	53.00 (2.23)	75.95 (2.31)
VIII	56.07 (2.35)	78.13 (2.36)

The spectral data are obtained in an aqueous solution unless otherwise stated. Figure 1 shows the spectra of complex I, *cis*-K[Co(ida)$_2$] and *trans*-K[Co(ida)$_2$]. The splitted first band of complex I suggests that it takes the *trans* structure with respect to the nitrogen atoms. As regard to these *trans* structures, two possible coordinating structures can be assumed, *i. e.*, facial configuration (Fig. 2 (A)) with respect to O–N–O and meridional one. However, the former seems to be more reasonable than the latter because the observations of NMR[5,6] and electronic spectra[9] and the consideration on the favorable bond angles[7] in the *trans* IDA or MDA complexes suggests that the *trans* facial is prefered to *trans* meridional configuration.

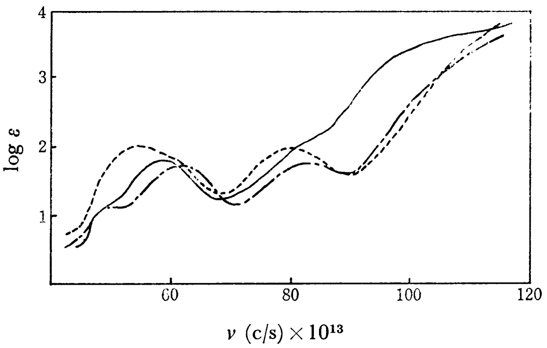

Fig. 1. Absorption spectra for complex I (——), *trans*-K[Co(ida)$_2$](— · —) and *cis*-K[Co(ida)$_2$] (·········).

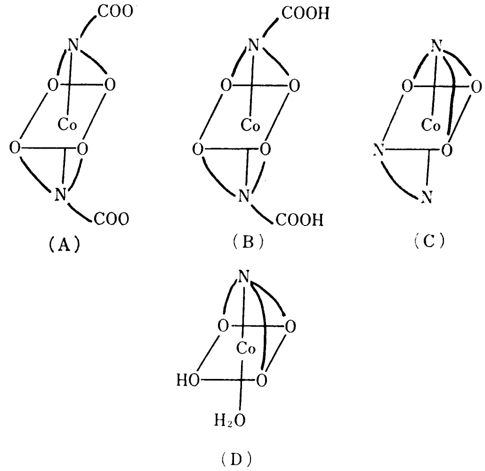

Fig. 2. Possible structures.

The shapes of the absorption bands of the complexes II, III and IV are essentially analogous to that of complex I. It is reasonable from these facts to consider that complexes II, III and IV may also have the *trans* structure. The IR data show the existence of free carboxylic acid in complexes II and IV, and they seem to have (B) structure as given in Fig. 2.

As for complexes V, VI and VIII, only the *mer* structure with respect to the nitrogen atoms as shown in Fig. 2 (C) can be considered.

Two possible coordinating structures are considered for the structure of complex VII. In the one, the OH group is situated in the *cis* position in relation to the nitrogen atoms of NIPDA, and in the other, in the *trans* position. It has been suggested that K[Co(OH)(nta)(H_2O)] has such two isomers; the isomer corresponding to the former was named α type (*cis*) and that corresponding to the latter named β type (*trans*).[1] Comparison of IR spectrum for Complex VII with that for the α or β type of NTA complex indicates that the spectrum of complex VII resembles the former type, and it would be better to assign the *cis* structure to complex VII as shown in Fig. 2 (D).

Comparison of the Properties of Cobalt(III)- with Those of Chromium(III)-Com-

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[14] D. H. Busch and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **75**, 4574 (1953).

[15] H. Yamatera, This Bulletin, **31**, 95 (1958).

[16] N. Matsuoka, J. Hidaka and Y. Shimura, This Bulletin, **40**, 1868 (1967).

plexes. It will be of interest to compare the difference in properties between the cobalt(III)- and the corresponding chromium(III) complexes.

It has been stated on the basis of electronic spectra that the chromium(III) complex corresponding to I is successively aquated as follows:

$$[Cr(nta)_2]^{3-} \rightarrow [Cr(OH)(nta)(H_2O)]^{-} \rightarrow [Cr(OH)(nta)(H_2O)_2]^{-}.^{2)}$$

Complex I does not undergo such an aquation. It has been found that the chromium(III) complex corresponding to complex VII turns from $[Cr(OH)(nipda)(H_2O)]^-$ to $[Cr(OH)(nipda)(H_2O)_2]^-$ in an aqueous solution.12) Complex VII does not show such a change. These facts suggest that the chromium(III) complexes more easily undergo an aquation than the corresponding cobalt(III) complexes in these cases, probably due to the stronger affinity of the metal ion aganist oxygen than aganist nitrogen in the chromium(III) complexes, and *vice versa* in cobalt(III) complexes.

The Coordination Behaviros of the Ligands Toward Chromium(III) or Cobalt(III) Ions. On the basis of the above consideration, the coordinating behaviors of NTA, NPDA and NIPDA toward the metals are summarized in Table 5. The symbol ○ means the possibility of coordination to metals and × the reverse. As seen in Table 5, all the ligands can act as N_1–O_3 type to both cobalt(III) and chromium(III). NIPDA can not behave as N_1–O_2 type for both metals. This may be due to some steric hindrance of CH_3 group and/or the lesser acidities of NIPDA than the other two. NPDA can not behave as O_3 type. This is because the ligand of the 5,5 and 6 membered rings (NPDA) makes the more stable complex than that of 5,5 and 5 membered rings (NTA and NIPDA).11,17) However, NTA and NIPDA can not act O_3 type to cobalt(III). This may mean that the cobalt has greater affinity to nitrogen than to oxygen.

Table 5. Chelating behaviors of ligands

Ligands	Type	Number of coordinated doner atoms	Chromium(III)	Cobalt (III)
NTA	N_1–O_3	4	○	○
	N_1–O_2	3	○	○
	O_3	3	○	×
NIPDA	N_1–O_3	4	○	○
	N_1–O_2	3	×	×
	O_3	3	○	×
NPDA	N_1–O_3	4	○	○
	N_1–O_2	3	○	○
	O_3	3	×	×

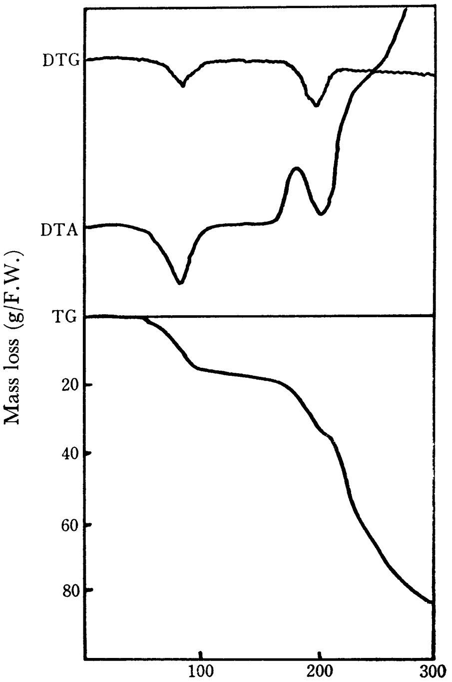

Fig. 3. Derivatogram for complex VII.

Observations of Thermal Decomposition Processes on Complex VII. The thermal decomposition processes of the complex VII were investigated by means of Derivatograph. The measurement was carried out in a constant nitrogen stream at a heating rate of 1°C/min. 500 mg of the samples was used. The derivatogram is shown in Fig. 3. Complex VII lost one mole of crystalline water at 100°C, and the mass loss corresponding to one mole of water is detected at *ca.* 180—200°C. It is of interest to note that the exothermic reaction is detected on DTA curve even in the dehydration process. At this step the color of the sample changed from bluish violet to reddish violet as in the case of the corresponding LDA complex (LDA: *l*-leucine-*N*,*N*-diacetic acid).18) From this result, it is considered that dimerization may occur at this step, and result in the formation of diol complex such as $K_2[(nipda)Co\genfrac{}{}{0pt}{}{\diagup OH \diagdown}{\diagdown OH \diagup}Co(nipda)]$.

The authors wish to thank the Ministry of Education for the financial support granted for this research.

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

18) A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **43**, 414 (1970).