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Derivatographic Studies on Transition Metal Complexes. XII.[1] Thermal Olation of Hydroxoaquo Cobalt(III) and Chromium(III) Complexes Containing Amino Acids in Solid Phase[2]

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The thermal olation of the following four types of complexes in a solid phase was investigated by means of derivatography: 1) cationic complexes, $[Co(OH)(n_3\text{-}o)(H_2O)]X$, 2) anionic complexes, $M[Co(OH)(n\text{-}o_3)(H_2O)]$, 3) double complexes, $[Co(OH)(n_3\text{-}o)(H_2O)][Co$ or $Cr(OH)(n\text{-}o_3)(H_2O)]$ and 4) neutral complexes, $[Co(OH)(n\text{-}o)_2(H_2O)]$, where n_3-o, n-o_3 and $(n\text{-}o)_2$ denote gly-en (glycinate ion and ethylenediamine) or dtma (diethylenetriaminemonoacetate ion), the analogues of nta (nitrilotriacetate ion) and α-amino acid ions, respectively. The thermal data such as initiation temperature, enthalpy change and activation energy of the olation were estimated from the respective derivatograms. From the results the effect of various ligands or counter ions (outer-sphere ions) on the olation was discussed.

Olation in a solid phase was first observed by Werner[3] in the $[Co(OH)(H_2O)(NH_3)_4]X_2$ type complexes. Recently, Wendlandt and Fisher reported that the olation of complexes of this type takes place endothermically and that the heats of olation are 3.3, 6.1, 4.2 and 2.4 kcal/mol for $X=Cl^-$, Br^-, NO_3^- and SO_4^{2-}, respectively.[4] It is of interest that the values are considerably smaller than those expected for the liberation of coordinated water alone. However, these values are understandable if the olation is considered to involve both dissociation of coordinated water and formation of olated compound simultaneously; the former step might be an endothermic, and the latter step an exothermic reaction.

In part IV of this series, we reported on the olation of the anionic complexes having the general formula $K[Co(OH)(n\text{-}o_3)(H_2O)]$,[5] where the ligand $(n\text{-}o_3)$ refers to nta, nipda, α-abda, vda, lda, pgda and pada.[6] The values of enthalpy change estimted from the DTA curves showed that the olation of all the anionic complexes proceeds exothermically. From an inspection of the numerical values of initiation temperature and activation energy, we concluded that the olation takes place more readily according to the sequence: nta→nipda→α-abda→vda→lda→pgda→pada-complexes.

The present study was undertaken to obtain information on the olation of various types of complexes and to systematically examine the effect of various ligands

1) Part XI of this series: R. Tsuchiya, T. Murakami, and E. Kyuno, This Bulletin, **46**, 3119 (1973).

2) Presented in part at the 26th Annual Meeting of the Chemical Society of Japan, Hiratsuka, 1, April, 1972.

3) A. Werner, *Ber.*, **40**, 4434 (1907).

4) W. W. Wendlandt and J. K. Fisher, *J. Inorg. Nucl. Chem.*, **24**, 1685 (1962).

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6) The full names are as follows : nta : nitrilotriacetate ion, nipda : nitriloisopropionicdiacetate ion, α-abda : *d,l*-α-amino-*n*-butyric-*N,N*-diacetate ion, vda : *l*-valine-*N,N*-diacetate ion, lda : *l*-leucine-*N,N*-diacetate ion, pgda : *d*-α-phenylglycine-*N,N*-diacetate ion and pada : *d,l*-α-phenylalanine-*N,N*-diacetate ion.

and counter ions (outer-sphere ions) on the olation. The thermal olation of cationic, anionic, double and neutral complexes was investigated by means of derivatography; it can be formulated as follows:

1) $2[Co(OH)(n_3\text{-}o)(H_2O)]X \rightarrow [(n_3\text{-}o)Co(OH)_2Co(n_3\text{-}o)]X_2 + 2H_2O$

2) a) $2K[Co(OH)(n\text{-}o_3)(H_2O)] \rightarrow K_2[(n\text{-}o_3)Co(OH)_2Co(n\text{-}o_3)] + 2H_2O$

b) $2M(I)$ *or* $M(II)_{1/2}[Co(OH)nipda(H_2O)] \rightarrow M(I)_2$ *or* $M(II)[(nipda)Co(OH)_2Co(nipda)] + 2H_2O$

3) $[Co(OH)(n_3\text{-}o)(H_2O)][Co$ *or* $Cr(OH)(n\text{-}o_3)(H_2O)] \rightarrow [(n_3\text{-}o)Co(OH)_2Co$ *or* $Cr(n\text{-}o_3)] + 2H_2O$

4) $2[Co(OH)(n\text{-}o)_2(H_2O)] \rightarrow [(n\text{-}o)_2Co(OH)_2Co(n\text{-}o)_2] + 2H_2O$

where n_3-o, n-o and n-o_3 denote gly-en (glycinate ion and ethylenediamine) or dtma (diethylenetriamine-monoacetate ion), α-amino acid ion and the analogues of nta ion, respectively, and M(I) and M(II) refer to any one of the alkali metal and the alkaline earth metal ions, respectively.

The hydroxoaquo-type complexes used as the starting materials are listed in Table 1 (The numerals refer to the index numbers of the respective complexes).

As cationic complexes, $[Co(OH)gly(H_2O)en]X$ and $[Co(OH)dtma(H_2O)]X$ were used, where X represents a univalent anion such as Cl^-, NO_3^-, Br^- and I^-.

Table 1. List of hydroxoaquo-type complexes used in the present study

	Type		General formula	Complex[a)]	Index No.
1.	Cationic complexes	1.	$[Co(OH)gly(H_2O)en]X$	[Co (gly en)]Cl·aq	1.1.1
				[Co (gly en)]NO_3·aq	1.1.2
				[Co (gly en)]Br	1.1.3
		2.	$[Co(OH)dtma(H_2O)]X$	[Co (dtma)]NO_3	1.2.1
				[Co (dtma)]Br·aq	1.2.2
				[Co (dtma)]I	1.2.3
2.	Anionic complexes	1.	$K[Co(OH)(n\text{-}o_3)(H_2O)]$	K[Co nta]·aq	2.1.1
				K[Co nipda]·2aq	2.1.2
				K[Co α-abda]·2aq	2.1.3
				K[Co vda]·1.5aq	2.1.4
				K[Co lda]·aq	2.1.5
				K[Co pada]·5aq	2.1.6
		2.	$M(I)[Co(OH)nipda(H_2O)]$	Li[Co nipda]·aq	2.2.1
				Na[Co nipda]·aq	2.2.2
				Rb[Co nipda]·aq	2.2.3
				Cs[Co nipda]	2.2.4
		3.	$M(II)_{1/2}[Co(OH)nipda(H_2O)]$	$Mg[Co\ nipda]_2$·2aq	2.3.1
				$Ca[Co\ nipda]_2$·2aq	2.3.2
				$Sr[Co\ nipda]_2$·2aq	2.3.3
				$Ba[Co\ nipda]_2$·4aq	2.3.4
3.	Double complexes	1.	$[Co(OH)gly(H_2O)en][Co(OH)(n\text{-}o_3)(H_2O)]$	[Co (gly en)][Co nta]·2aq	3.1.1
				[Co (gly en)][Co nipda]·2aq	3.1.2
				[Co (gly en)][Co α-abda]·2aq	3.1.3
				[Co (gly en)][Co vda]·2aq	3.1.4
				[Co (gly en)][Co lda]·2aq	3.1.5
				[Co (gly en)][Co pada]·2aq	3.1.6
			$[Co(OH)gly(H_2O)en][Cr(OH)(n\text{-}o_3)(H_2O)]$	[Co (gly en)][Cr nta]·2aq	3.1.7
				[Co (gly en)][Cr nipda]·2aq	3.1.8
				[Co (gly en)][Cr α-abda]·2aq	3.1.9
				[Co (gly en)][Cr vda]	3.1.10
				[Co (gly en)][Cr lda]·2aq	3.1.11
				[Co (gly en)][Cr pada]·2aq	3.1.12
		2.	$[Co(OH)dtma(H_2O)][Co(OH)(n\text{-}o_3)(H_2O)]$	[Co (dtma)][Co nta]·2aq	3.2.1
				[Co (dtma)][Co nipda]·2aq	3.2.2
				[Co (dtma)][Co α-abda]·2aq	3.2.3
				[Co (dtma)][Co vda]·2aq	3.2.4
				[Co (dtma)][Co lda]·2aq	3.2.5
				[Co (dtma)][Co pada]·2aq	3.2.6
			$[Co(OH)dtma(H_2O)][Cr(OH)(n\text{-}o_3)(H_2O)]$	[Co (dtma)][Cr nta]·4aq	3.2.7
				[Co (dtma)][Cr nipda]·4aq	3.2.8
				[Co (dtma)][Cr α-abda]·2aq	3.2.9
				[Co (dtma)][Cr vda]·2aq	3.2.10
				[Co (dtma)][Cr lda]·4aq	3.2.11
				[Co (dtma)][Cr pada]·2aq	3.2.12
4.	Neutral complexes		$[Co(OH)(n\text{-}o)_2(H_2O)]$	$[Co\ (gly)_2]$·2aq	4.1
				$[Co\ (ala)_2]$·aq	4.2

n-o_3 and n-o denote the analogues of nta ion and α-amino acid ions, respectively.

a) OH and H_2O are omitted in all the formulas.

For the anionic complexes, all the ligands (n-o_3) used can form (5,5,5)-membered chelate rings and their structures become more bulky according to the order: nta→nipda→α-abda→vda→lda→pgda→pada.

Two kinds of double complexes were obtained, one containing cobalts as the central metal both in cationic and anionic species (designated as [Co][Co]), and the other containing cobalt in cationic and chromium in anionic species (designated as [Co][Cr]). The double complexes are especially interesting for carrying out studies from the viewpoint of 1) whether the olation takes place between two identically charged complex ions or between two counter charged complex ions, and 2) the difference in olation to be found between [Co][Co] and [Co][Cr].

Neutral complexes are advantageous for observing the net olation because of the lack of counter ions.

Experimental

Preparation of Materials. *1) Cationic Complexes. Hydroxoglycinatoaquoethylenediaminecobalt(III) Perchlorate, [Co(OH)gly(H_2O)en]ClO_4 (reddish violet).* Eight grams of the chloroaquo complex ([CoCl(gly)(H_2O)en]Cl[7]) was dissolved in 25 ml of aqueous solution containing 1.5 g of sodium hydroxide. The solution was mildly heated at 50 °C on a water-bath until the violet solution turned dark red. Special care should be taken to prevent the temperature of the solution from exceeding 50 °C, otherwise an undesirable diaquo complex is frequently generated. Twenty-five milliliters of water containing 14 g of sodium perchlorate was added to the dark red solution. Gentle heating was continued until the color turned bright reddish violet. As soon as reddish violet crystals began to appear, the solution was cooled in a refrigerator. A pH value of 10—11 was suitable for obtaining the desired complex. The crystals were recrystallized from water. Yield 2 g

The corresponding chloride, nitrate and bromide were prepared by the same procedure except that sodium chloride, sodium nitrate and sodium bromide were used, respectively, in place of sodium perchlorate.

Found: C, 14.11; H, 4.37; N, 12.91%. Calcd for [Co(OH)gly(H_2O)en]ClO_4: C, 14.67; H, 4.61; N, 12.83%.

Hydroxodiethylenetriaminemonoacetatoaquocobalt(III) Perchlorate, [Co(OH)dtma(H_2O)]ClO_4 (reddish violet). The complex was prepared by a method similar to that for [Co(OH)gly(H_2O)en]ClO_4 except that the dichloro complex ([$CoCl_2$-dtma][8,9]) was used as the starting material in place of [CoCl(gly)(H_2O)en]Cl. Twenty-nine grams of the dichloro complex was dissolved in 200 ml of aqueous solution containing 6 g of sodium hydroxide. The solution was gently heated at 50 °C on a water-bath until the violet solution turned dark red. To this solution was added 14 g of sodium perchlorate. The solution was again concentrated by gentle heating (50 °C) until reddish violet crystals were separated out. Another crop of crystals was obtained by cooling the solution. The product was recrystallized from water. Yield 5 g.

The corresponding nitrate, bromide and iodide were prepared by the same procedure except that sodium nitrate, sodium bromide and sodium iodide were used, respectively, instead of sodium pechlorate.

Found: C, 21.36; H, 4.74; N, 11.69%. Calcd for [Co(OH)dtma(H_2O)]ClO_4: C, 20.92; H, 5.11; N, 11.83%.

2) Anionic Complexes. K[Co(OH)nta(H_2O)]·H_2O,[10] K[Co(OH)nipda(H_2O)]·$2H_2O$,[11] K[Co(OH)α-abda(H_2O)]·$2H_2O$,[12] K[Co(OH)vda(H_2O)]·$1.5H_2O$,[12] K[Co(OH)lda(H_2O)]·H_2O,[13] K[Co(OH)pada(H_2O)]·$5H_2O$,[14] K[Cr(OH)nta(H_2O)]·$2H_2O$,[15] K[Cr(OH)nipda(H_2O)]·$2H_2O$,[16] K[Cr(OH)α-abda(H_2O)]·$2H_2O$,[17] K[Cr(OH)vda(H_2O)]·$2H_2O$,[17] K[Cr(OH)lda(H_2O)]·$3H_2O$[13] and K[Cr(OH)pada(H_2O)]·$5H_2O$[14] were prepared by the procedures described in the respective references.

Li, Na, Rb and Cs salts of the M(I)[Co(OH)nipda(H_2O)] type and Mg, Ca, Sr and Ba salts of the M(II)[Co(OH)nipda(H_2O)]$_2$ type were synthesized by similar way to that for K[Co(OH)nipda(H_2O)]·$2H_2O$[11] except that lithium carbonate, sodium bicarbonate, rubidium carbonate, cesium carbonate, magnesium carbonate, calcium carbonate, strontium carbonate and barium carbonate were used, respectively, in place of potassium bicarbonate.

3) Double Complexes. The procedure is a simple one. After 0.1 mmol of the hydroxoaquo cationic and anionic complexes were dissolved separately in 100 ml of hot aqueous solution, the two solutions were mixed together. On cooling, the double complexes were immediately separated out as violet crystals.

Although double complexes, in general, have low solubility, they can be recrystallized from a large amount of hot water. These complexes were obtained almost stoichiometrically.

4) Neutral Complexes. Hydroxobis(glycinato)aquocobalt(III) Dihydrate, [Co(OH)gly_2(H_2O)]·$2H_2O$ (violet). Twenty three grams of cobalt(II) chloride hexahydrate was dissolved in 100 ml of water. Fifteen grams of glycine was neutralized with 100 ml of water containing 8 g of sodium hydroxide. The two solutions were mixed and 10 ml of 28% hydrogen peroxide solution of was then added in order to oxidize the cobalt(II) ion. The solution was gently heated on a water-bath. Violet crystals gradually separated out during the heating. A pH value of 9—10 was suitable for obtaining the desired compound. The compound could not be recrystallized since it was sparingly soluble in ordinary solvents. However, chemical analysis showed that it is highly pure.

Found: C, 17.59; H, 5.14; N, 10.20%. Calcd for [Co(OH)gly_2(H_2O)]·$2H_2O$: C, 17.27; H, 5.43; N, 10.07%.

Hydroxobis(α-alaninato)aquocobalt(III) Monohydrate, [Co(OH)ala_2(H_2O)]·H_2O (violet). The complex was prepared by a procedure similar to that for [Co(OH)gly_2(H_2O)]·$2H_2O$ except that 18 g of α-alanine was used in place of glycine. It was also violet and insoluble in any solvent. Thus, recrystallization could not be carried out.

Found: C, 24.78; H, 5.69; N, 9.52%. Calcd for [Co(OH)-ala_2(H_2O)]·H_2O: C, 25.01; H, 5.95; N, 9.72%.

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13) A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 414 (1970).

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

17) To be published elsewhere.

Derivation of [Co(gly)dtma]ClO_4 from [Co(OH)dtma(H_2O)]-ClO_4. Four grams of [Co(OH)dtma(H_2O)]ClO_4 was dissolved in 200 ml of water to which was added 50 ml of water containing 1 g of glycine. The solution was warmed on a water-bath at 30—40 °C until the color of the solution turned red from reddish violet. The pH of the resulting solution was 4—5. The solution was allowed to stand in a refrigerator overnight. Red crystals were obtained. The crystals were recrystallized from water.

Found: C, 21.78; H, 5.04; N, 12.34%. Calcd for [Co(gly) dtma]ClO_4: C, 21.49; H, 4.96; N, 12.54%.

Instruments The electronic spectra of an aqueous solution of the complexes were measured with a Hitachi EPS spectrophotometer, and those of a finely-powdered solid with a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment. The far-infrared spectra were measured in a Nujol-mull state with a Hitachi EPI-1 type infrared spectrophotometer. The effective magnetic moments were evaluated from the magnetic susceptibilities measured by the Gouy method. A derivatograph Typ-OD-102 was used for observation on the thermal decomposition processes of each sample. The analyses of the derivatograms obtained were carried out as reported previously.[18]

Results and Disucssion

Structures of Complexes. Cationic Complexes: It is clear from the chelate structure (nta or its analogues) that the anionic complexes must have the *cis* form with respect to the position of OH^- and H_2O. On the other hand, several possible isomers are feasible for the structures of both cationic complexes [Co(OH)-gly(H_2O)en]X and [Co(OH)dtma(H_2O)]X. The geometrically possible isomers for [Co(OH)gly(H_2O)en]$^+$ and [Co(OH)dtma(H_2O)]$^+$ are shown in Fig. 1. In order to identify their structures, the derivative syntheses of [Co(gly)$_2$en]X and [Co(gly)dtma)]X from [Co(OH)gly(H_2O)en]X and [Co(OH)dtma(H_2O)]X, respectively, were attempted under mild conditions. For the dtma-complex, the procedure for deriving [Co(gly)dtma]ClO_4 from [Co(OH)dtma(H_2O)]ClO_4 is given as an example (see Experimental). Under such preparative conditions,[7,8] the original structure in the mother complex may be retained through the reaction path way.

The electronic spectra of [Co(gly)$_2$en]ClO_4 and [Co(gly)dtma]ClO_4 are shown in Fig. 2. A splitting can be detected at the higher frequency side of the first band in both spectra. It is known that the complex giving the above splitting should have the *trans*(O) form.[7] Thus, both the mother complexes can be concluded to have the mer(N)-*cis*(OH,H_2O) form (Fig. 1).

Neutral Complexes. Four geometrically possible isomers considered for [Co(OH)(n-o)$_2$(H_2O)] are shown in Fig. 3. The electronic spectrum of [Co(OH)gly$_2$-(H_2O)]·2H_2O (4.1) is shown in Fig. 4. If the complex takes *trans*(N) form, the spectrum should have a splitting in the first band. However, no splitting was observed. Thus, the *trans*(N) form is discarded. In addition, the *cis* form with respect to the position of OH and H_2O is also readily verified by the fact that the complex easily undergoes olation. Thus, Structure A (Fig. 3) may be reasonably accepted for the complex. The same is also true for [Co(OH)-ala$_2$(H_2O)]·H_2O (4.2).

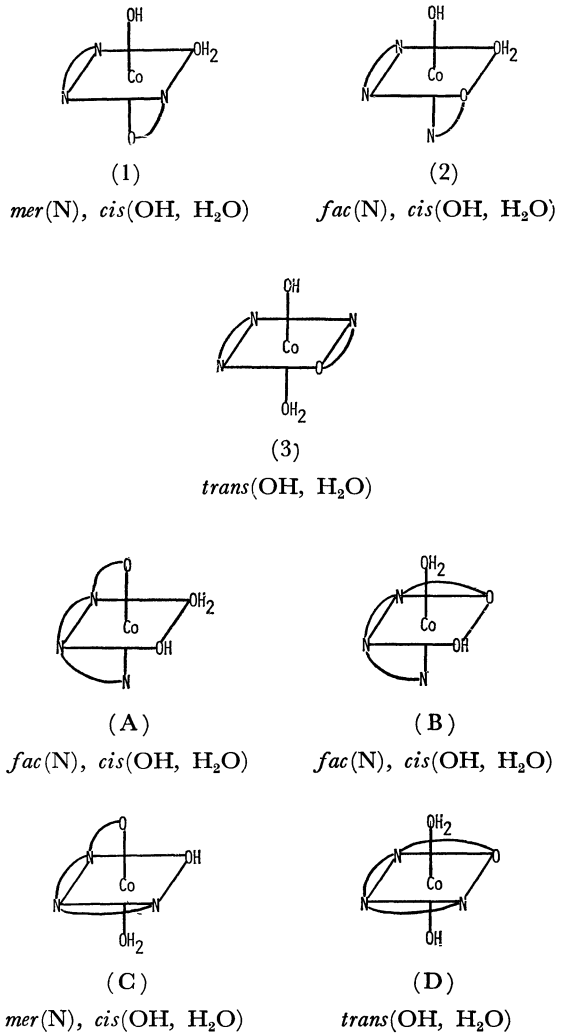

Fig. 1. Geometrically possible isomers of [Co(OH)gly(H_2O)-en]$^+$ and [Co(OH)dtma(H_2O)]$^+$.

Observation on Thermal Decomposition Processes by Derivatograph. Thermal decomposition processes were observed by using a derivatograph. In order to obtain fine derivatograms which permit us to separately detect the individual thermal reaction process, preliminary experiments were carried out by using samples of various grain sizes, 50—100, 100—200 and more than 200 mesh, respectively, and by applying the heating rates of 1, 3, 5 and 10 °C/min. The particle sizes within the above ranges were found to have no substantial effect on the shape of all the thermal curves. However, the degree of resolution of DTA peak was lowered when the heating rate exceeded 3 °C/min. Thus, all the measurements were carried out at a heating rate of 1 °C/min with a constant rate of nitrogen stream. Samples were triturated into 100—200 mesh in an agate mortar, and 500 mg of them was used in each run.

18) R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, This Bulletin, **42**, 1881 (1969).

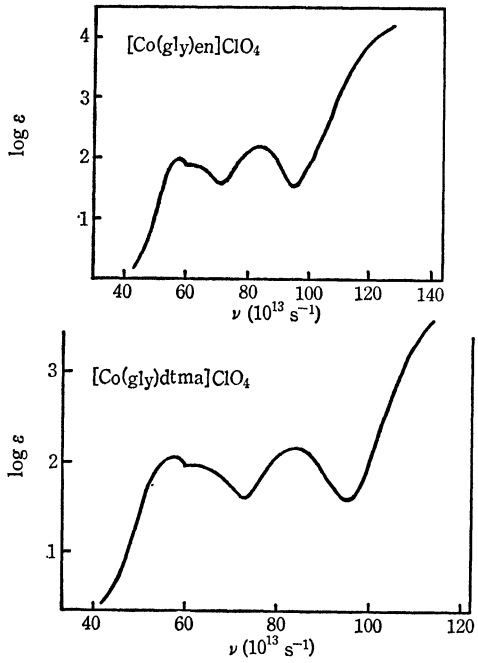

Fig. 2. Electronic spectra of $[Co(gly)_2en]ClO_4$ and $[Co(gly)dtma]ClO_4$ derived from the hydroxoaquo-type complexes.

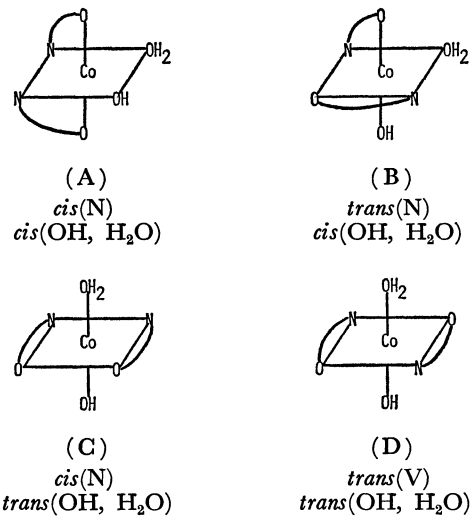

Fig. 3. Geometrically possible isomers of $[Co(OH)(n\text{-}o)_2(H_2O)]$.

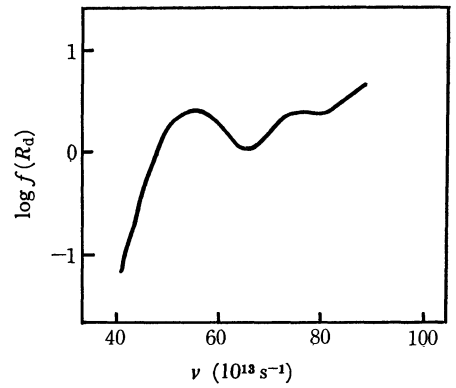

Fig. 4. Electronic spectrum of $[Co(OH)gly_2(H_2O)]\cdot 2H_2O$ (4.1).

The derivatograms for $[Co(OH)gly(H_2O)en]Cl\cdot H_2O$ (1.1.1), $[Co(OH)dtma(H_2O)]Br\cdot H_2O$ (1.2.2) and $K[Co(OH)lda(H_2O)]\cdot H_2O$ (2.1.5) as the representatives of the cationic and anionic complexes are shown in Fig. 5. As seen in the TG curve of $K[Co(OH)lda(H_2O)]\cdot H_2O$ (2.1.5), the mass losses corresponding to one mole of water are detected at *ca.* 60 and 175 °C. The former step corresponds to the liberation of crystalline water, the latter to the olation due to the removal of coordinated water. The color turned pink from bluish violet in the latter step, where an exothermic

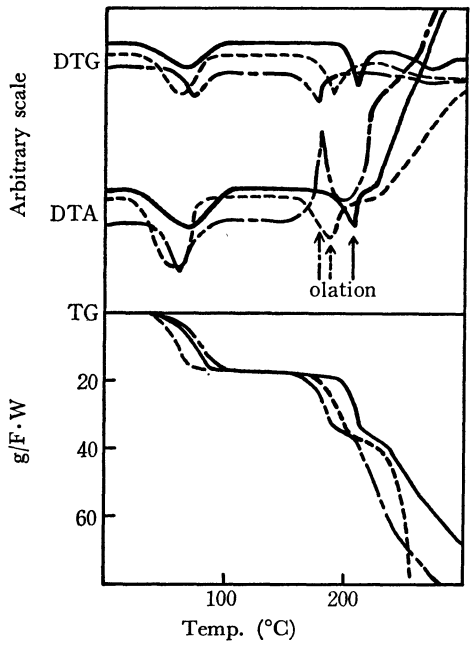

Fig. 5. Derivatograms for $[Co(OH)gly(H_2O)en]Cl\cdot H_2O$ (1.1.1)(----), $[Co(OH)dtma(H_2O)]Br\cdot H_2O$ (1.2.2)(——), and $K[Co(OH)lda(H_2O)]$(2.1.5)(——).

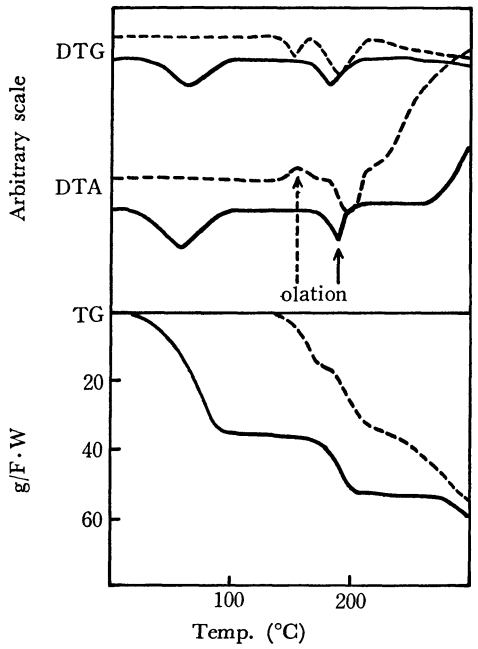

Fig. 6. Derivatograms for $K[Co(OH)nta(H_2O)]\cdot H_2O$ (2.1.1) (----) and $[Co(OH)gly_2(H_2O)]\cdot 2H_2O$(4.1)(——).

DTA peak appears. Such a change was observed in all the anionic complexes. However, the case is different with K[Co(OH)nta(H_2O)]·H_2O (2.1.1), the derivatogram of which is shown in Fig. 6 together with that of the neutral complex, [Co(OH)gly_2(H_2O)]·2H_2O (4.1). In the case of K[Co(OH)nta(H_2O)]·H_2O (2.1.1), although the two steps of mass losses corresponding to one mole of water were separately observed at *ca.* 150 and 175 °C, the color change was found in the former step, with an exothermic DTA peak. The former step is thus thought to correspond to the olation and the latter to the liberation of crystalline water.

The cationic complex [Co(OH)gly(H_2O)en]Cl·H_2O (1.1.1) lost one mole of water at both 37 and 166 °C. The original reddish violet color turned pink in the latter step. Olation seems to take place in this step as a consequence of the liberation of the coordinated water. The thermal decomposition process of [Co(OH)dtma(H_2O)]Br·H_2O (1.2.2) was essentially similar to that of [Co(OH)gly(H_2O)en]Cl·H_2O (1.1.1). The olation in both cationic complexes was endothermic in contrast to that of the anionic complexes as seen in DTA curves, Fig. 5.

As for the olation of the neutral complexes, an endothermic peak was detected as in the DTA curve of [Co(OH)gly_2(H_2O)]·2H_2O (4.1).

Since there is a striking contrast between the DTA curves of the cationic and anionic complexes, it is of interest to observe the olation of the double complexes. The derivatograms for [Co(OH)gly(H_2O)en][Co(OH)pada(H_2O)]·2H_2O (3.1.6), [Co(OH)gly(H_2O)en][Cr(OH)pada(H_2O)]·2H_2O (3.1.12) and [Co(OH)dtma(H_2O)][Co(OH)pada(H_2O)]·2H_2O (3.2.6) are shown in Fig. 7. All three complexes lose each two moles of water in two separate steps. In the latter step, the color of [Co(OH)gly(H_2O)en]-[Co(OH)pada(H_2O)]·2H_2O (3.1.6) and [Co(OH)-dtma(H_2O)][Co(OH)pada(H_2O)]·2H_2O (3.2.6) turned pink from violet while that of [Co(OH)gly(H_2O)en]-[Cr(OH)pada(H_2O)]·2H_2O (3.1.12) brownish pink from violet. The color change is probably due to the consequent olation.

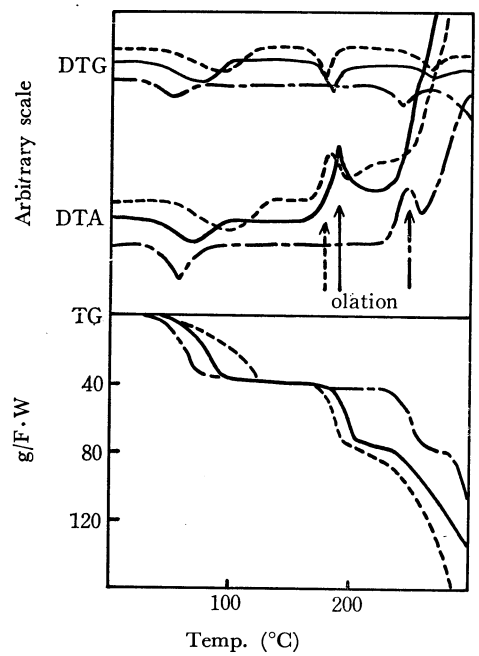

Fig. 7. Derivatograms for [(Co(OH)gly(H_2O)en][Co(OH)-pada(H_2O)]·2H_2O (3.1.6)(----), [Co(OH)gly(H_2O)en][Cr-(OH)pada(H_2O)]·2H_2O (3.1.12)(——) and [Co(OH)-dtma(H_2O)][Co(OH)pada(H_2O)]·2H_2O (3.2.6)(——).

Electronic Spectra. It is well-known that cobalt(III) complexes containing "ol" groups show a specific band due to the bridged OH groups at about 100×10^{13} s^{-1}, the second band being frequently concealed by the strong specific band.[19]

The specific band could not be directly detected for all the complexes after heating since it was experimentally impossible to measure the electronic spectra beyond 90×10^{13} s^{-1} in a solid state. However, the obscurity of the second band of all the complexes after heating indicates that the specific band due to the bridged OH groups probably remains in the region of about 100×10^{13} s^{-1}.

Far-Infrared Spectra. In general, the hydroxoaquo complexes give bands at 640, 570 and 535 cm^{-1} in the region 700—500 cm^{-1}, and the diol complexes at 630, 545 and 505 cm^{-1}. All the hydroxoaquo complexes after heating at the above temperatures give spectra similar to those of the diol complexes. Thus, the results suggest the conversion of the hydroxoaquo complexes into the corresponding diol complexes upon heating.

From a study on the far-infrared spectrum of [$(NH_3)_4$-$Co(OH)_2Co(NH_3)_4$]$(SO_4)_2$·2H_2O in the CsBr region, it is presumed that the strong band at 530—540 cm^{-1} is due to the presence of the four-membered cobalt-oxygen ring (–$Co(OH)_2Co$–).[20] The band of the diolcomplexes which appears at 545 cm^{-1} might be a characteristic band due to the skeletal vibration of –$Co(OH)_2Co$–.

Magnetic Moments. In order to examine the valency state of the central metal ions, the effective magnetic moments (μ_{eff}) were calculated from the magnetic susceptibilities measured at an ambient temperature by the Gouy method.

As for K[Co(OH)(n-o_3)(H_2O)], M(I) or $M(II)_{1/2}$-[Co(OH)(nipda)(H_2O)], [Co(OH)(n_3-o)(H_2O)]X and [Co(OH)(n_3-o)(H_2O)][Co(OH)(n-o_3)(H_2O)] type complexes, all the complexes were diamagnetic both before and after heating. On the other hand, the magnetic moments of [Co(OH)(n_3-o)(H_2O)][Cr(OH)(n-o_3)-(H_2O)] type complexes were 3.8—3.9 B.M., which is very close to the spin-only value of tervalent chromium ion. The actual change in magnetic moments could not be detected after heating.

The results indicate that both chromium and cobalt ions in all the complexes are tervalent, no actual electron transfer taking place upon heating. However, it is not clear whether or not such an electron transfer is generated in a step of the overall heating processes.

Thermochemical Data. The enthalpy changes (ΔH) of the olation of all the complexes were estimated from the DTA peak area.[18] The Arrhenius activation

19) Y. Inamura and Y. Kondo, *Nippon Kagaku Zasshi*, **74**, 627 (1953).

20) G. Blyholder and N. Ford, *J. Phys. Chem.*, **68**, 1496 (1964).

Table 2. Thermochemical data for olation

Type of complex	Index No. of complex	Initiation Temp. (°C)	ΔH (kcal/mol)	E_A (kcal/mol)
Cationic complexes	1.1.1	166	13.6	70.7
	1.1.2	175	1.8	82.1
	1.1.3	180	10.4	84.2
	1.2.1	188	1.7	82.9
	1.2.2	175	10.5	93.5
	1.2.3	194	8.7	97.2
Anionic complexes	2.1.1	150	−1.2	29.7
	2.1.2	195	−4.8	85.8
	2.1.3	185	−6.3	75.4
	2.1.4	175	−12.8	70.8
	2.1.5	175	−14.3	65.1
	2.1.6	170	−21.3	62.8
	2.2.1	193	−5.5	84.0
	2.2.2	188	−4.9	82.5
	2.2.3	189	−4.0	84.2
	2.2.4	188	−5.5	84.5
	2.3.1	223		
	2.3.2	225		
	2.3.3	221		
	2.3.4	230		
Neutral complexes	4.1	184	3.6	83.5
	4.2	164	7.0	48.6
Double complexes	3.1.1	188	8.3	97.6
	3.1.2	162	−1.5	69.5
	3.1.3	177	−4.2	73.9
	3.1.4	167	−8.8	57.9
	3.1.5	167	−9.9	54.9
	3.1.6	162	−14.6	53.4
	3.1.7	205	8.9	89.9
	3.1.8	220	7.3	94.4
	3.1.9	229	0.8	93.5
	3.1.10	225	−5.5	96.7
	3.1.11	230	−8.2	101.5
	3.1.12	230	−10.6	98.7
	3.2.1	180	10.0	80.2
	3.2.2	176	4.7	68.6
	3.2.3	175	−7.5	70.8
	3.2.4	167	−9.1	55.9
	3.2.5	167	−14.3	54.3
	3.2.6	165	−17.2	37.1
	3.2.7	205	8.2	80.8
	3.2.8	203	11.5	71.7
	3.2.9	205	−1.6	83.5
	3.2.10	210	−5.2	90.3
	3.2.11	217	−8.6	99.2
	3.2.12	217	−11.5	100

energies (E_A) of the reaction were calculated from the slope of the Arrhenius plots derived by the analysis of DTA or DTG curve.[18] The detailed analysis of DTA or DTG curve confirmed that the olation of all the complexes proceeds in a first-order. The numerical values of the thermochemical data are summarized in Table 2. For the sake of simplification, some of the data obtained are diagramatically plotted as in Figs. 8 (A) through (F). In the abscissa, the outer sphere ions or the ligands (n-o_3) are taken at regular intervals in the order of the increase of radius or volume, while the initiation temperatures (T), the enthalpy changes (ΔH) and the Arrhenius activation energies (E_A) are plotted in the ordinate.

1) Cationic Complexes. We see from Fig. 8 (A) that the initiation temperature rises with the size of the outer sphere ions (for example, in the case of [Co(OH)gly(H_2O)en]X, $Cl^- < NO_3^- < Br^-$), and the same tendency is also observed in the activation energies. This means that the increase in the anion size reduces the ease of olation. The enthalpy changes for the nitrate salts [Co(OH)gly(H_2O)en]$NO_3 \cdot H_2O$ (1.1.2) and [Co(OH)dtma(H_2O)]NO_3 (1.2.1) are significantly smaller as compared with those for the other complexes. This may be due to the fact that the nitrate salts are decomposed just after the olation takes place and the heat of olation overlaps that of the subsequent decomposition. A comparison of [Co(OH)gly(H_2O)-en]X with [Co(OH)dtma(H_2O)]X reveals that both the initiation temperatures and the activation energies of the latter type complexes are somewhat higher than those of the former except for the initiation temperature of the bromide salts. This suggests that olation takes place more readily with [Co(OH)gly(H_2O)en]X than with [Co(OH)dtma(H_2O)]X.

2) Anionic Complexes. Figure 8 (B) illustrates the diagramatical relation of the thermochemical data when the ligands (n-o_3) are varied against the fixed cation (K). Fig. 8 (C) and (D) show the corresponding data when the cations are varied against the fixed ligand (nipda).

As seen from Fig. 8 (B), the exothermic heat of olation shows an increasing trend with the structural complexity of the ligands (n-o_3). On the other hand, a decreasing trend is found in the values of E_A except for that of K[Co(OH)nta(H_2O)]$\cdot H_2O$ (2.1.1). Accordingly, it is conceivable that the olation easily takes place in the order: nipda→pada-complexes and the nta-complex can be most easily olated.

Since the M(II)[Co(OH)nipda(H_2O)]$_2$ type complexes decomposed just after the olation took place and their fine derivatograms could not be obtained, the ΔH and E_A could not be estimated. Thus the initiation temperatures alone are given in Table 2 and Fig. 8 (D). From a comparison of the data for the M(I) *or* M(II)$_{1/2}$[Co(OH)nipda(H_2O)], K[Co(OH)(n-o_3)(H_2O)] and [Co(OH)(n_3-o)(H_2O)]X type complexes, it follows that the thermochemical data found when cations (M(I) and M(II)) are varied are not so greatly affected as those obtained when the ligands (n-o_3 and n_3-o) or the anions are varied. This suggests that the effect of cations on the olation is smaller than that of anions or ligands. The initiation temperatures of the M(II)$_{1/2}$[Co(OH)nipda(H_2O)] type complexes are considerably higher than those of the M(I)[Co(OH)nipda(H_2O)] type complexes. The reason might be attributed to the difference of the crystal structures.

3) Neutral Complexes. The data for [Co(OH)-gly$_2$(H_2O)]$\cdot 2H_2O$ (4.1) and [Co(OH)ala$_2$(H_2O)]$\cdot H_2O$ (4.2) indicate a tendency for the latter to give rise to olation more easily than the former.

4) Double Complexes. In the case of the [Co]-[Co] type complexes, as shown in Fig. 8 (E), the initiation temperatures and the activation energies decrease in the order of the complexity in the structure of the n-o_3 ligands: nta-→pada-complexes. The tendency is compatible with that found in the case of the anionic complexes.

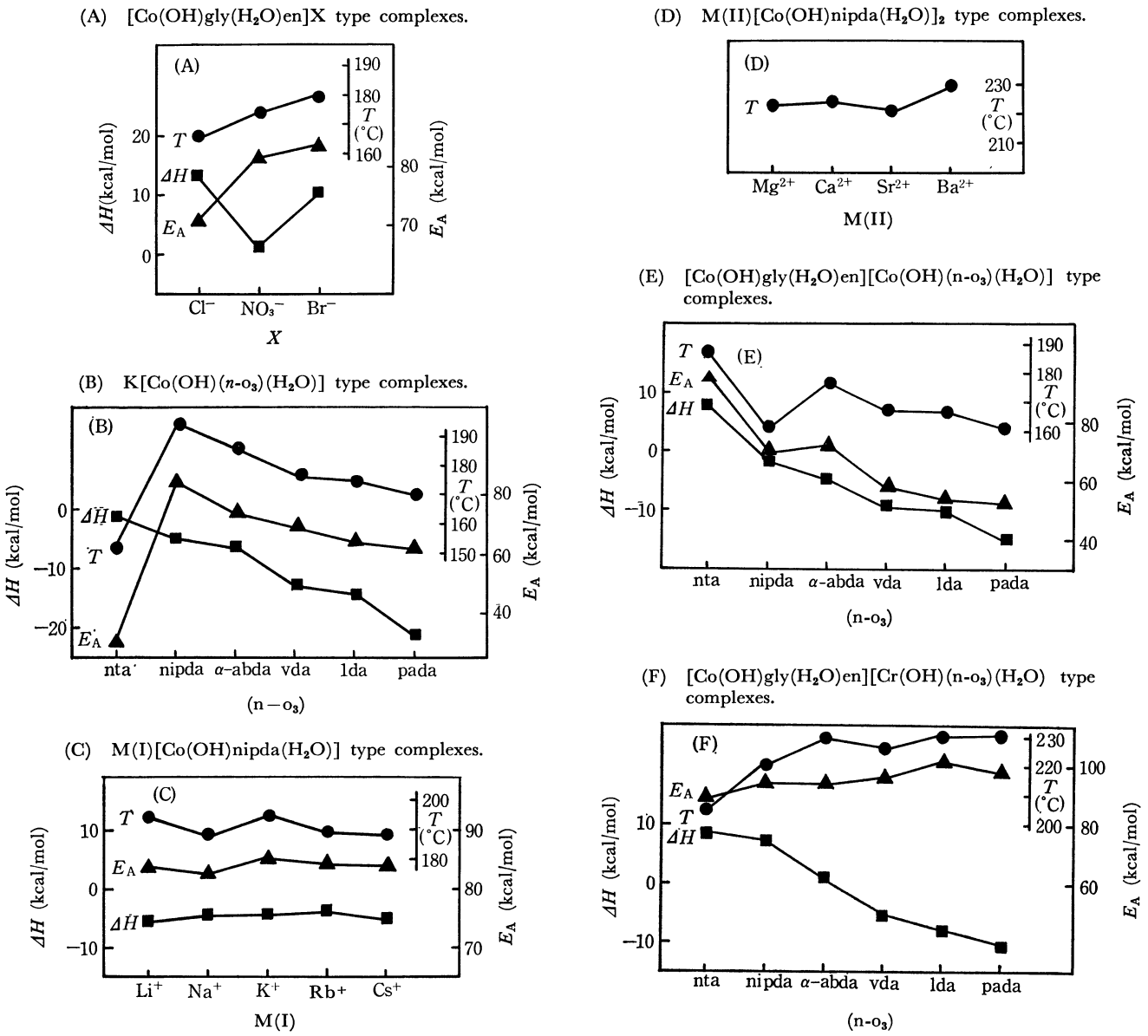

Fig. 8. Diagrammatical relation of thermochemical data.

In contrast, in the case of the [Co][Cr] type complexes a distinct tendency is not observed, but we see that the values of the initiation temperatures and the activation energies become to some extent higher in the order: nta-→pada-complexes. This indicates that the olation readily takes place in the order: pada-→nta-complexes, differing from the case of the [Co][Co] complexes.

The enthalpy changes for the olation of the anionic complexes show a decreasing trend with the complexity in the structures of the n-o_3 ligands: nta-→pada-complexes. On the other hand, the enthalpy changes accompanied by the olation of the double complexes are uniformly larger than those of the respective anionic complexes. Thus, it might be concluded that the values of ΔH for the olation of the double complexes are approximately proportional to the sum of the values for the cationic and anionic complexes; *i.e.*, ΔH_d (for double complex)$=\Delta H_c$ (for cationic complex)$+\Delta H_a$ (for anionic complex).