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Derivatographic Studies on Transition Metal Complexes. XVI.[1] Thermal Chelation of Na[CoX(Hedta or Hpdta)] and $[CoX(Hgly)en_2]X_2$ ($X=Cl^-$ or Br^-) Type Complexes in Solid Phase[2]

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Thermal chelation of the following two types of complexes in solid phase was investigated by means of derivatography: Na[CoX(Hedta or Hpdta)] and $[CoX(Hgly)en_2]X_2$ ($X=Cl^-$ or Br^-), where Hedta or Hpdta and Hgly designate quinquedentate ethylenediaminehydrogentetraacetate or propylenediaminehydrogentetraacetate ion and unidentate glycine molecule, respectively. The results show that all the complexes undergo characteristic thermal chelation through the dehydrohalogenation, giving an increase in ligand denticity from five to six in Na[CoX(Hedta or Hpdta)] and one to two in $Na[CoX(Hgly)en_2]X_2$. The reaction mechanism in the thermal chelation of each complex in solid phase was discussed in terms of the thermochemical data.

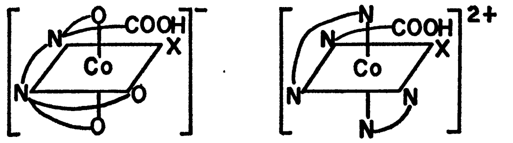
In some complexes where multidentate ligand coordinates to metal ion with its partial denticity, the potential multidenticity can be completely satisfied by further occupying the other coordination sites vacated by the escape of volatile molecule upon heating.

Such a change in which the increase of ligand denticity is involved is designated as "thermal chelation" in this paper. The situation may easily arise when the atom entering into the coordination site to form chelation in multidentate ligand resides near the escapable ligand such as H_2O or NH_3. As an example, Hertzenberg and Bailar found[3] that the unidentate sulfato complexes *cis*-$[Co(SO_4)(H_2O)(NH_3)_4]X$ ($X=ClO_4^-$, BF_4^- or $1/2PtCl_6^{2-}$) are deaquated to form the bidentate sulfato complexes $[Co(SO_4)(NH_3)_4]X$ at temperatures in the range 110—160 °C upon heating. Another example of the reaction was also reported on the quinquedentate EDTA complex $[Cr(Hedta)(H_2O)]$ and on the terdentate NPDA (nitrilopropionicdiacetic acid) complex $[Cr(OH)(Hnpda)(H_2O)_2]$: the former was converted into sexidentate EDTA complex H[Cr(edta)] and the latter into quadridentate NPDA complex $[Cr(npda)(H_2O)_2]$ with the increase of ligand denticity through deaquation by heating.[4]

In this paper, we deal with the thermal chelation of two additional types of complexes, Na[CoX(Hedta or Hpdta)] and $[CoX(Hgly)en_2]X_2$ ($X=Cl^-$ or Br^-), where Hedta, Hpdta and Hgly designate quinquedentate EDTA and PDTA and unidentate glycine molecule, respectively. These two types of thermal chelation are essentially distinguished from those mentioned above[3,4] with respect to the involvement of "dehydrohalogenation" in place of "dehydration".

Experimental

Preparation of Complexes. Both types of complexes used as the starting materials are characterized (Fig. 1), by the coordination of a halide ion and of quinquedentate diaminocarboxylate anion or unidentate amino acid molecule, the latter containing an uncoordinated -COOH group. They easily evolve the hydrogen halide formed from H^+ in -COOH and X^- in the coordination sphere upon heating.



Na[CoX(Hedta or Hpdta)] $[CoX(Hgly)en_2]X_2$

Fig. 1. Structure of the complexes used.

Quinquedentate EDTA and PDTA Complexes: $Na[CoCl(Hedta)]\cdot 2H_2O$, Na[CoBr(Hedta)], $Na[CoCl(Hpdta)]\cdot 2H_2O$ and $Na[CoBr(Hpdta)]\cdot 1/2H_2O$. They were prepared according to the procedures described in literature.[5–7]

Unidentate Glycine Complexes: $[CoCl(Hgly)en_2]Cl_2$ and $[CoBr(Hgly)en_2]Br_2$. They were synthesized by the method of Alexander and Busch[8] modified as folllows.

$[CoCl(Hgly)en_2]Cl_2$. *trans*-$[CoCl_2en_2]Cl$ (2.9 g, 0.01 mol) and ethyl glycinate (1.4 g, 0.01 mol) were placed in a mortar together with water (3 ml) and diethylamine (1 ml). The mixture was triturated sufficiently to form red aggregates, which were suspended in ethanol and then collected by filtration.[9] To the ethyl glycinato complex (1 g, 0.003 mol) thus obtained was added 4 M hydrochloric acid (13 ml) to hydrolyze it and isopropyl alcohol (18 ml) was dropped into the resulting red solution, which was left to stand overnight in a refrigerator. Reddish voilet crystals were obtained and recrystallized from a minimum amount of hot water. Yield 0.5 g.

Found: C, 19.8; H, 6.2; N, 19.3%. Calcd for $[Co(C_6H_{21}N_5O_2Cl)]Cl_2$: C, 20.0; H, 5.9; N, 19.4%.

$[CoBr(Hgly)en_2]Br_2$. The complex was prepared by a procedure analogous to that for the above complex except that *trans*-$[CoBr_2en_2]Br$, triethylamine and 7 M hydrobromic acid solution were used in place of *trans*-$[CoCl_2en_2]Cl$, diethylamine and 4 M hydrochloric acid solution, respectively. Recrystallization was carried out from hydrobromic acid solution. From 1 g of the starting glycinato complex $[CoBr(NH_2CH_2COOC_2H_5)en_2]Br_2$ was obtained 0.2 g of the product.

Found: C, 14.7; H, 4.8; N, 13.9%. Calcd for $[Co(C_6H_{21}N_5O_2Br)]Br_2$: C, 14.6; H, 4.3; N, 14.2%.

Measurements. The thermal reactions of the complexes under non-isothermal conditions were observed with a MOM Derivatograph Typ-OD-102,[10] and those under isothermal conditions were measured with a Shimadzu

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TM-1A thermanobalance or an Abderhalden's apparatus. The IR and UV spectra of the samples obtained at the various heating steps were measured in Nujol-mull state with JASCO model IR-E and Hitachi EPS spectrophotometers.

Results and Discussion

In order to visually grasp the thermal chelation in EDTA, PDTA and glycine complexes, experimental results obtained with Na[CoBr(Hedta)] and [CoCl(Hgly)en$_2$]Cl$_2$ are given as the typical examples.

Derivatography. Figure 2 gives the derivatograms of Na[CoBr(Hedta)] and [CoCl(Hgly)en$_2$]Cl$_2$. The TG curve of Na[CoBr(Hedta)] shows that each half mole of HBr is evolved at 53—105 °C and at 105—145 °C, respectively, the DTA curve giving two endothermic peaks in the range corresponding to the evolution of each half mole of HBr. The original bluish violet color of the complex turned violet at the final stage of dehydrobromination.

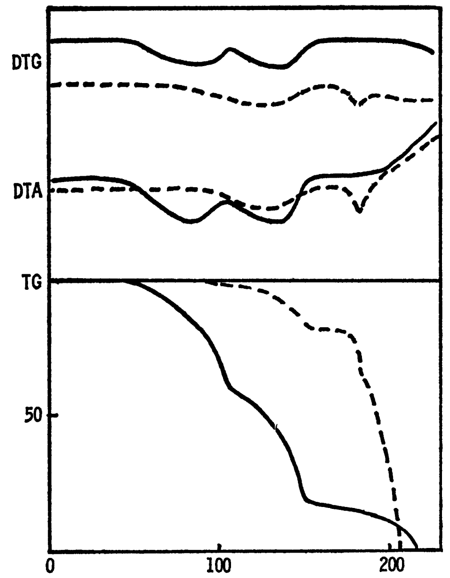
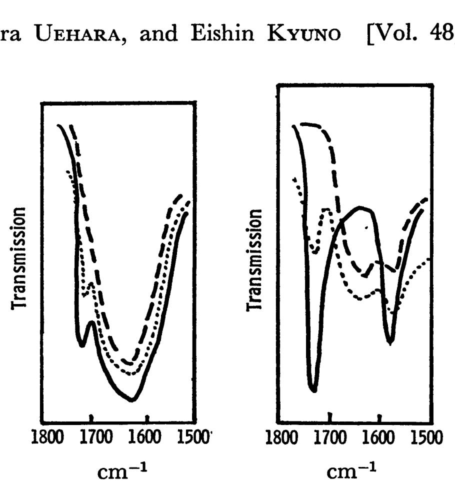


Fig. 2. Derivatograms of Na[CoBr(Hedta)](——) and [CoCl(Hgly)en$_2$]Cl$_2$(----).

In the case of [CoCl(Hgly)en$_2$]Cl$_2$, the complex releases at first a half mole of HCl at 75—150 °C and then decomposes rapidly at 175 °C as shown in its TG curve. However, a reflection and a small endothermic peak are observed in TG and DTA curves, respectively, at the point which gives the weight loss corresponding to the liberation of a further half mole of HCl. Although the formation of the stable intermediate product can not be confirmed distinctly, the color of the original complex turned orange red from reddish violet after complete dehydrobromination. The isothermal measurement also showed that the original complex brings about the complete dehydrobromination to form the bidentate glycinato-complex [Co(gly)en$_2$]Cl$_2$ upon heating at 150 °C for 10 hr.



(a) (b)

Fig. 3. (a) IR spectra of Na[CoBr(Hedta)](——) and its products obtained upon heating at 105 °C (······) and at 145 °C (----).
(b) IR spectra of [CoCl(Hgly)en$_2$]Cl$_2$ (——) and its products obtained upon heating at 150 °C (······) and upon heating isothermally at 150 °C for 10 hr (----).

IR Spectra. Figure 3 shows the changes of the ν_{CO} in Na[CoBr(Hedta)] and [CoCl(Hgly)en$_2$]Cl$_2$. Na[CoBr(Hedta)] gave a sharp band at 1730 cm^{-1} and a broad one at 1600—1700 cm^{-1} before heating, the former being assigned to $\nu_{C=O}$ of free carboxylic acid (–COOH) and the latter to that of the coordinated carboxylate group (–COO–Co).[11] The IR spectral pattern obtained in the sample heated at 105 °C does not essentially differ from that of the original one, the sharp band at 1730 cm^{-1} disappearing in the sample heated at 145 °C. This indicates that free carboxylic acid in the complex participated in coordination as a consequence of complete dehydrobromination, thermal chelation thus taking place. On the other hand, [CoCl(Hgly)en$_2$]Cl$_2$ still gave a sharp band at 1740 cm^{-1} due to the presence of free –COOH besides the band at 1580 cm^{-1} attributable to the δ_{NH_2} of glycinate ion. However, the sharp band disappeared in the sample isothermally heated at 150 °C for 10 hr, while a band due to the presence of –COO–Co appeared at 1600—1700 cm^{-1}. This suggests that the unidentate glycine complex was now converted into the bidentate glycinato-complex through complete dehydrochlorination, thermal chelation taking place.

Electronic Spectra. Figure 4 shows the electronic spectra of aqueous solutions of Na[CoBr(Hedta)], the complex heated at 145 °C and the reference complex Na[Co(edta)]·2H$_2$O prepared by the method in literature.[12] The absorption maxima of Na[CoBr(Hedta)] heated at 145 °C appear in relatively higher frequency region as compared with those of the original complex Na[CoBr(Hedta)], and closely resemble those of the reference complex. This also indicates that the original complex was converted into Na[Co(edta)] by dehydrobromination accompanied by thermal chelation.

A similar change in electronic spectra is recognized in the case of [CoCl(Hgly)en$_2$]Cl$_2$ (Fig. 5); the complex heated isothermally at 150 °C for 10 hr gives essentially the same spectrum as that of the reference complex [Co(gly)en$_2$]Cl$_2$.[8]

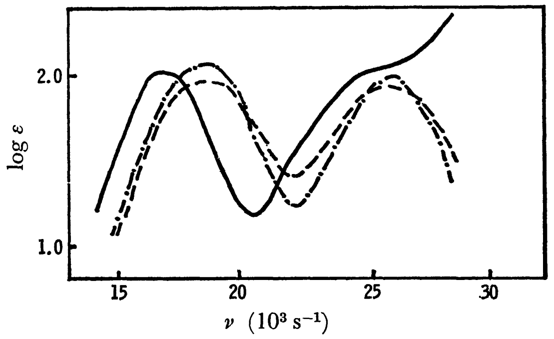


Fig. 4. Electronic spectra of Na[CoBr(Hedta)] (——), its product obtained upon heating at 145 °C (----) and the reference complex, Na[Co(edta)]·2H$_2$O (—·—).

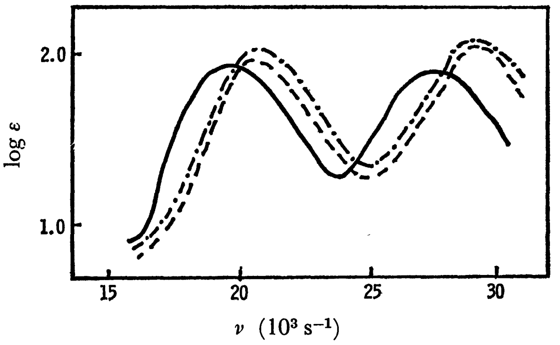
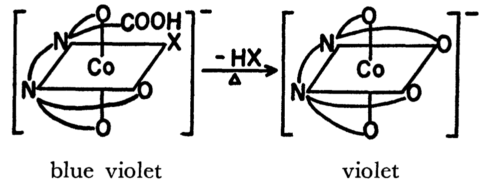
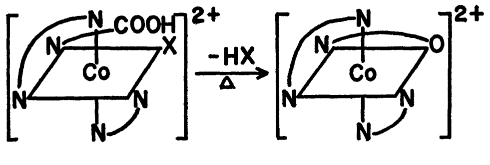


Fig. 5. Electronic spectra of [CoCl(Hgly)en$_2$]Cl$_2$ (——), its product obtained upon heating at 150 °C for 10 hr (----) and the reference complex, [Co(gly)en$_2$]Cl$_2$·H$_2$O (—·—).



(a) Na[CoX(Hedta or Hpdta)]



(b) [CoX(Hgly)en$_2$]X$_2$

Fig. 6. Schemes of thermal chelation of Na[CoX(Hedta or Hpdta)] (a) and (CoX(Hgly)en$_2$)X$_2$ (b).

This is another evidence supporting the following conversion.

$$[CoCl(Hgly)en_2]Cl_2 \xrightarrow[\Delta]{} [Co(gly)en_2]Cl_2 + HCl$$

Measurement of magnetic susceptibilities showed that the cobalt ion in all the complexes remained as a tervalent state throughout the dehydrohalogenation process. The reaction seems to proceed according to the schemes shown in Fig. 6.

Thermochemical Data. Thermochemical data such as initiation temperatures, enthalpy changes (ΔH) and activation energies (E_a) were estimated in order to study the effect of kinds of ligands or counter ions on thermal chelation.

Na[CoX(Hedta or Hpdta)] Type Complexes. The enthalpy change of the reaction was estimated from the DTA peak area in the derivatograms and the activation energy from the slope of Arrhenius plots derived from the analysis of the DTA or DTG curve.[10] The numerical values of the thermochemical data are summarized in Table 1.

TABLE 1. THERMOCHEMICAL DATA FOR THERMAL CHELATION OF Na[CoX(Hedta or Hpdta)] TYPE COMPLEXES

Complex		Init. Temp °C	ΔH kcal/mol	E_a kcal/mol
Na[CoCl(Hedta)]·2H$_2$O	1st	97	17.4	28.3
	2nd	103	17.0	57.0
Na[CoCl(Hpdta)]·2H$_2$O	1st	110	19.2	21.5
	2nd	181	18.3	116
Na[CoBr(Hedta)]	1st	53	26.4	29.2
	2nd	105	22.5	30.8
Na[CoBr(Hpdta)]·1/2H$_2$O	1st	92	20.8	40.8
	2nd	108	19.2	129

1st and 2nd denote the first (1/2 mol) and the second (1/2 mol) liberation steps, respectively, of the dehydrohalogenation.

The values of the enthalpy changes for the first and second dehydrohalogenation steps are approximately in the same order, but the value of the activation energy for the first step almost exceeds that for the second step in each complex. This suggests that the evolution of the first half mole of hydrogen halide and that of the second half mole of it proceed *via* different mechanisms though the details are still unknown.

The enthalpy changes for the bromo-complexes are relatively greater than those for the chloro-complexes and the same tendency is also recognized in the activation energies except for the second step of Na[CoCl(Hedta)]·2H$_2$O. This reflects the fact that thermal chelation of the bromo-complexes takes place with more difficulty than that of chloro-complexes. This can be understood in terms of data of the bond energies[13] as follows.

From the bond energies of O–H, 110.6, H–Cl, 103.2 and H–Br, 87.5 kcal mol^{-1}, the energy required for the bond rupture between O and H subtracted by the energy evolved in the bond formation between H and Br, ΔH=15.7 kcal mol^{-1}, is larger than the corresponding value concerning H and Cl, 7.4 kcal mol^{-1}. These two values are in line with those of the enthalpy changes in the thermal chelation of Na[CoBr(Hedta or Hpdta)] and Na[CoCl(Hedta or Hpdta)], respectively.

Comparison of the enthalpy changes and the avtivation energies for the EDTA-complexes with the corresponding data for the PDTA-complexes reveals that the former complexes undergo thermal chelation more easily than the latter.

$[CoX(Hgly)en_2]X_2$ Type Complexes. Although the occurrence of thermal chelation could be confirmed by measurements of infrared and electronic spectra, no plateau distinctly indicating the formation of the intermediate products could be observed in the TG curve. Thus, no reliable thermal data were available from DTA and DTG peak analyses.

So far as the complexes $[CoX(Hgly)en_2]X_2$ are concerned, the activation energies for the thermal chelation were estimated by the isothermal measurement in the following manner. The sample was heated at each temperature of 140, 147, 152, and 164 °C for 150 min and the compositions of the products were determined spectrophotometrically. Since the absorbancies of the original complex $[CoCl(Hgly)en_2]Cl_2$ and the reference complex $[Co(gly)en_2]Cl_2 \cdot H_2O$ are 33.3 and 11.4 at 580 nm, and 62.5 and 106.4 at 484 nm, respectively, the composition of samples in each product by thermal chelation was calculated by means of the following simultaneous equations:

$$33.3x + 11.4y = D_{580}$$

$$62.6x + 106.4y = D_{484},$$

where x and y are the concentrations of the original complex and the complex formed by the thermal chelation, respectively, and D_{580} and D_{484} are the absorbancies at 580 and 484 nm, respectively. The chelation ratios, $[CoCl(Hgly)en_2]/[Co(gly)en_2]$ therefore, are given by $y/(x+y)$. Similar procedures were also employed for the bromo-complex. The rate constant k for thermal chelation was obtained by the chelation ratio. The activation energies were estimated from slope of the Arrhenius plots derived from the relationship of log k *vs.* $1/T$.

The values of 32.4 and 26.1 kcal mol^{-1} were obtained as the activation energies for the chloro- and the bromo-complexes, respectively. It might be said that the thermal chelation of the bromo-complex takes place more easily than that of the chloro-complex. This tendency is in contrast to that for the EDTA- and PDTA-complexes, the reason being not clear as yet.

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