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A Calorimetric Study on the Relative Thermal Stability of Some Bis(diamine)cobalt(III) Complexes in a Solid Phase

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The enthalpy changes (ΔH) in the reaction of *trans*-$[CoX_2(AA)_2]X \cdot mHX \cdot nH_2O$-type complexes with an alkaline sodium sulfide solution were calorimetrically measured at 25 °C, where AA is diamine and X is Cl^-, Br^-, or ClO_4^-; $m=0$ or 1, and $n=0$, 0.5, 1, or 2. The thermal stabilities were found to decrease in the following orders for both dichloro and dibromo complexes: 1,2-ethanediamine>*l*- or *d*-1,2-propanediamine>racemic 1,2-propanediamine, *d,l*-2,3-butanediamine>meso-2,3-butanediamine>2-methyl-1,2-propanediamine, 1,2-ethanediamine> 1,3-propanediamine, and *meso*-2,4-pentanediamine>*d,l*-2,4-pentanediamine. The complexes containing six-membered diamine chelate rings were less stable than those containing five-membered diamine chelate rings. The dibromo complex bromides were less stable than the corresponding dichloro complex chlorides.

Neither trans-to-cis nor cis-to-trans isomerization has so far been found in the solid $[CoX_2en_2]X$-type complexes (X: Cl^- or Br^-). Our previous paper, however, calorimetrically predicted that the above complexes undergo cis-to-trans isomerization in a solid phase, and the prediction was actually verified.[1] The enthalpy change was predominant relative to the entropy change in the free energy change of the above isomerization. The relative thermal stability among the trans-complexes in a solid phase is, therefore, considered to depend principally upon the difference in enthalpy changes of complex formation from each component in a gaseous state. On the basis of such idea, the strain energy calculation by conformational analysis has been carried out by many workers[2] for mono-, bis- and tris-diamine Co(III), Mo(0), Cr(III), Cr(0), Pt(II), and Pd(II) complexes. On the other hand, the relative strain enthalpies have been obtained calorimetrically by Woldbye *et al.*[3] for some tris(diamine)cobalt(III) complexes in an aqueous solution. The strain enthalpies by conformational analysis and by calorimetry have never been obtained for these diamine complexes in a solid phase. In the present study, the thermal stability of $[CoX_2(AA)_2]X \cdot mHX \cdot nH_2O$-type complexes in a solid phase was discussed on the basis of lattice energies evaluated from the enthalpy changes for the reaction with an alkaline sodium sulfide solution, where AA is a diamine, *m* is 0 or 2, and *n* is 0, 0.5, 1, or 2.

Experimental

Preparation of Diamines. 1,2-Ethanediamine (en), 1,2-propanediamine (pn), and 1,3-propanediamine (tn) were commercially available. 2,3-Butanediamines (*dl*-bn and *m*-bn)[4] and 2,4-pentanediamines (*dl*-ptn and *m*-ptn)[5] were prepared by the literature methods and characterized by NMR spectra.[6,7] 2-Methyl-1,2-propanediamine (*i*-bn) was supplied by Aldrich Chemical Co. Inc.

Preparation of Complexes. The following complexs were prepared by the literature methods slightly modified: *trans*-$[CoCl_2en_2]Cl \cdot HCl \cdot 2H_2O$, *trans*-$[CoCl_2en_2]Cl$,[8] *trans*-$[CoCl_2pn_2]Cl \cdot HCl \cdot 2H_2O$, *trans*-$[CoCl_2pn_2]Cl \cdot H_2O$, *trans*-$[CoCl_2(l\text{-pn})_2]Cl \cdot H_2O$,[9] *trans*-$[CoCl_2(dl\text{-bn})_2]ClO_4$, *trans*-$[CoCl_2(m\text{-bn})_2]ClO_4$, *trans*-$[CoCl_2(i\text{-bn}_2)]ClO_4$,[5] *trans*-$[CoCl_2tn_2]Cl$,[10] *trans*-$[CoCl_2(dl\text{-ptn})_2]Cl \cdot 0.5H_2O$, *trans*-$[CoCl_2(m\text{-ptn})_2]Cl \cdot 0.5H_2O$,[11] *trans*-$[CoBr_2en_2]Br \cdot HBr \cdot 2H_2O$, *trans*-$[CoBr_2en_2]Br$,[12] *trans*-$[CoBr_2pn_2]Br \cdot HBr \cdot 2H_2O$, *trans*-$[CoBr_2pn_2]Br \cdot H_2O$, *trans*-$[CoBr_2(d\text{-pn})_2]Br \cdot H_2O$,[9] *trans*-$[CoBr_2(dl\text{-bn})_2]ClO_4$, *trans*-$[CoBr_2(m\text{-bn})_2]ClO_4$, *trans*-$[CoBr_2(i\text{-bn})_2]ClO_4$,[5] *trans*-$[CoBr_2tn_2]Br$,[10] *trans*-$[CoBr_2(dl\text{-ptn})_2]Br \cdot 0.5H_2O$, and *trans*-$[CoBr_2(m\text{-ptn})_2]Br \cdot 0.5H_2O$.[11]

Calorimetric Measurements. The enthalpy changes in the reaction of the complexes in the powder state with an alkaline sodium sulfide solution were measured with a Tokyo-Riko twin isoperibol calorimeter TIC-2S at 25 °C. In each run, the diamine complexes were accurately weighed and the reacting solution was 100 cm³ of a mixture containing 2×10^{-2} mol dm⁻³ Na_2S and 1 mol dm⁻³ NaOH.

Results and Discussion

Thermal Stability of $[CoX_2(AA)_2]X \cdot mHX \cdot nH_2O$*-type Complexes with Various Diamines.* The enthalpy changes measured for the reaction of these complexes with an alkaline sodium sulfide solution are summarized in Table 1. The enthalpy changes for *trans*-$[CoCl_2en_2]Cl \cdot HCl \cdot 2H_2O1$ and *trans*-$[CoCl_2pn_2]Cl \cdot HCl \cdot 2H_2O$, are given as below,

$$\begin{gathered} trans\text{-}[CoCl_2en_2]Cl \cdot HCl \cdot 2H_2O(s) + 3/2\ S^{2-}(aq) + OH^-(aq) \\ = 1/2\ Co_2S_3(s) + 4Cl^-(aq) + 2en(aq) + 3H_2O(l) \\ \Delta H = -117.4\ \text{kJ mol}^{-1}, \end{gathered} \tag{1}$$

$$\begin{gathered} trans\text{-}[CoCl_2pn_2]Cl \cdot HCl \cdot 2H_2O(s) + 3/2\ S^{2-}(aq) + OH^-(aq) \\ = 1/2\ Co_2S_3(s) + 4Cl^-(aq) + 2pn(aq) + 3H_2O(l) \\ \Delta H = -136.7\ \text{kJ mol}^{-1}. \end{gathered} \tag{2}$$

On the other hand, the heats of dissolution of diamines into an alkaline sodium sulfide solution in the same concentration as above were also measured with the calorimeter, and their heats of vaporization were calculated from the boiling points and Trouton's constants. The values for en and pn are as follows:

$$\left.\begin{aligned} en(l) &= en(aq) & \Delta H &= -30.4\ \text{kJ mol}^{-1} \\ en(l) &= en(g) & \Delta H &= 34.3\ \text{kJ mol}^{-1} \end{aligned}\right\}, \tag{3}$$

$$\left.\begin{aligned} pn(l) &= pn(aq) & \Delta H &= -33.4\ \text{kJ mol}^{-1} \\ pn(l) &= pn(g) & \Delta H &= 34.5\ \text{kJ mol}^{-1} \end{aligned}\right\}. \tag{4}$$

Combining these values with those of Eqs. 1 and 2, the enthalpy change for the reaction,

$$\begin{gathered} trans\text{-}[CoCl_2en_2]Cl \cdot HCl \cdot 2H_2O(s) + 2pn(g) \\ = trans\text{-}[CoCl_2pn_2]Cl \cdot HCl \cdot 2H_2O(s) + 2en(g), \end{gathered}$$

TABLE 1. ENTHALPY CHANGES, ΔH, FOR THE REACTION OF COBALT(III) COMPLEXES WITH SODIUM SULFIDE SOLUTION

Complex	$X=Cl^-$ ΔH/kJ mol^{-1}	$X=Br^-$ ΔH/kJ mol^{-1}
trans-$[\mathrm{CoX_2en_2}]\mathrm{X\cdot HX\cdot 2H_2O}$	−117.4	−89.8
trans-$[\mathrm{CoX_2en_2}]\mathrm{X}$	−60.5	−40.5
trans-$[\mathrm{CoX_2pn_2}]\mathrm{X\cdot HX\cdot 2H_2O}$	−136.7	−107.7
trans-$[\mathrm{CoX_2pn_2}]\mathrm{X\cdot H_2O}$	−70.1	−64.3
trans-$[\mathrm{CoX_2}(l\text{-pn})_2]\mathrm{X\cdot H_2O}$	−65.1	—
trans-$[\mathrm{CoX_2}(d\text{-pn})_2]\mathrm{X\cdot H_2O}$	—	−59.1
trans-$[\mathrm{CoX_2}(dl\text{-bn})_2]\mathrm{ClO_4}$	−69.8	−73.0
trans-$[\mathrm{CoX_2}(m\text{-bn})_2]\mathrm{ClO_4}$	−81.2	−80.5
trans-$[\mathrm{CoX_2}(i\text{-bn})_2]\mathrm{ClO_4}$	−84.0	−85.4
trans-$[\mathrm{CoX_2tn_2}]\mathrm{X}$	−89.6	−57.5
trans-$[\mathrm{CoX_2}(dl\text{-ptn})_2]\mathrm{X\cdot 0.5H_2O}$	−121.0	−87.9
trans-$[\mathrm{CoX_2}(m\text{-ptn})_2]\mathrm{X\cdot 0.5H_2O}$	−101.9	−80.5

TABLE 2. ENTHALPY CHANGES, ΔH, FOR THE SUBSTITUTION REACTION OF DIAMINE

Substitution reaction	$X=Cl^-$ ΔH/kJ mol^{-1}	$X=Br^-$ ΔH/kJ mol^{-1}
trans-$[\mathrm{CoX_2\underline{en_2}}]\mathrm{X\cdot HX\cdot 2H_2O}\rightarrow\mathrm{\underline{pn_2}}$$^{a)}$	12.9	11.5
trans-$[\mathrm{CoX_2\underline{en_2}}]\mathrm{X}\rightarrow\mathrm{\underline{tn_2}}$	17.9	5.8
trans-$[\mathrm{CoX_2}(\underline{l\text{-pn}}\text{ or }\underline{d\text{-pn}})_2]$-$\mathrm{X\cdot H_2O}\rightarrow\mathrm{\underline{pn_2}}$	5.0	5.2
trans-$[\mathrm{CoX_2}(\underline{dl\text{-bn}})_2]\mathrm{ClO_4}\rightarrow(\underline{m\text{-bn}})_2$	9.6	5.7
trans-$[\mathrm{CoX_2}(\underline{dl\text{-bn}})_2]\mathrm{ClO_4}\rightarrow(\underline{i\text{-bn}})_2$	14.2	12.4
trans-$[\mathrm{CoX_2}(\underline{m\text{-ptn}})_2\mathrm{X\cdot 0.5H_2O}\rightarrow(\underline{dl\text{-ptn}})_2$	20.5	8.8

a) Represents the substitution reaction, *trans*-$[\mathrm{CoX_2en_2}]\mathrm{X\cdot HX\cdot 2H_2O(s)+2pn(g)}$ = *trans*-$[\mathrm{CoX_2pn_2}]\mathrm{X\cdot HX\cdot 2H_2O(s)+2en(g)}$. Such expressions are similarly used for the respective reactions.

was calculated as $\Delta H=12.9$ kJ mol^{-1}. The enthalpy change in substituting pn for en in the corresponding bromide was obtained as $\Delta H=11.5$ kJ mol^{-1} in the same way. These values should correspond to the difference in lattice energies between the bis(en) and bis(pn) complexes in chlorides and bromides. Thus, the bis(pn) complexes are thermally less stable than the corresponding bis(en) complexes (Table 2).

In order to compare the thermal stability between the complexes containing racemic pn and optically active *l*-pn or *d*-pn, the enthalpy changes for the following reactions were calculated by using the data in Table 1 and those in Eq. 4:

$$\textit{trans}\text{-}[\mathrm{CoCl_2pn_2}]\mathrm{Cl\cdot H_2O(s)} + 2(l\text{-pn})(\mathrm{g})$$
$$= \textit{trans}\text{-}[\mathrm{CoCl_2}(l\text{-pn})_2]\mathrm{Cl\cdot H_2O(s)} + 2\mathrm{pn(g)}$$
$$\Delta H = -5.0\ \mathrm{kJ\ mol^{-1}},$$
$$\textit{trans}\text{-}[\mathrm{CoBr_2pn_2}]\mathrm{Br\cdot H_2O(s)} + 2(d\text{-pn})(\mathrm{g})$$
$$= \textit{trans}\text{-}[\mathrm{CoBr_2}(d\text{-pn})_2]\mathrm{Br\cdot H_2O(s)} + 2\mathrm{pn(g)}$$
$$\Delta H = -5.2\ \mathrm{kJ\ mol^{-1}}.$$

These data suggest that the complexes containing optically active pn are thermally more stable than those containing racemic pn in both the chloride and the bromide.

By similar calculations, the enthalpy changes for the following reactions substituting tn for en were obtained:

$$\textit{trans}\text{-}[\mathrm{CoCl_2en_2}]\mathrm{Cl(s)} + 2\mathrm{tn(g)}$$
$$= \textit{trans}\text{-}[\mathrm{CoCl_2tn_2}]\mathrm{Cl(s)} + 2\mathrm{en(g)}$$
$$\Delta H = 17.9\ \mathrm{kJ\ mol^{-1}},$$
$$\textit{trans}\text{-}[\mathrm{CoBr_2en_2}]\mathrm{Br(s)} + 2\mathrm{tn(g)}$$
$$= \textit{trans}\text{-}[\mathrm{CoBr_2tn_2}]\mathrm{Br(s)} + 2\mathrm{en(g)}$$
$$\Delta H = 5.8\ \mathrm{kJ\ mol^{-1}}.$$

Here, the following data,

$$\mathrm{tn(l)} = \mathrm{tn(aq)} \qquad \Delta H = -34.4\ \mathrm{kJ\ mol^{-1}},$$
$$\mathrm{tn(l)} = \mathrm{tn(g)} \qquad \Delta H = 35.9\ \mathrm{kJ\ mol^{-1}},$$

were used. These data show that the bis(tn)cobalt(III) complexes with six-membered chelate rings are thermally less stable than the corresponding bis(en)cobalt(III) complexes with five-membered chelate rings in a solid phase.

By using the following data,

$$dl\text{-bn(l)} = dl\text{-bn(aq)} \qquad \Delta H = -35.9\ \mathrm{kJ\ mol^{-1}},$$
$$dl\text{-bn(l)} = dl\text{-bn(g)} \qquad \Delta H = 35.9\ \mathrm{kJ\ mol^{-1}},$$
$$m\text{-bn(l)} = m\text{-bn(aq)} \qquad \Delta H = -37.1\ \mathrm{kJ\ mol^{-1}},$$
$$m\text{-bn(l)} = m\text{-bn(g)} \qquad \Delta H = 35.6\ \mathrm{kJ\ mol^{-1}},$$
$$i\text{-bn(l)} = i\text{-bn(aq)} \qquad \Delta H = -36.2\ \mathrm{kJ\ mol^{-1}},$$
$$i\text{-bn(l)} = i\text{-bn(g)} \qquad \Delta H = 35.6\ \mathrm{kJ\ mol^{-1}},$$

the enthalpy changes for the following reactions were calculated:

$$\textit{trans}\text{-}[\mathrm{CoX_2}(dl\text{-bn})_2]\mathrm{ClO_4(s)} + 2m\text{-bn(g)}$$
$$= \textit{trans}\text{-}[\mathrm{CoX_2}(m\text{-bn})_2]\mathrm{ClO_4(s)} + 2dl\text{-bn(g)},$$
$$\text{for X} = \mathrm{Cl^-} \qquad \Delta H = 9.6\ \mathrm{kJ\ mol^{-1}},$$
$$\text{for X} = \mathrm{Br^-} \qquad \Delta H = 5.7\ \mathrm{kJ\ mol^{-1}},$$
$$\textit{trans}\text{-}[\mathrm{CoX_2}(dl\text{-bn})_2]\mathrm{ClO_4(s)} + 2i\text{-bn(g)}$$
$$= \textit{trans}\text{-}[\mathrm{CoX_2}(i\text{-bn})_2]\mathrm{ClO_4(s)} + 2dl\text{-bn(g)},$$
$$\text{for X} = \mathrm{Cl^-} \qquad \Delta H = 14.2\ \mathrm{kJ\ mol^{-1}},$$
$$\text{for X} = \mathrm{Br^-} \qquad \Delta H = 12.4\ \mathrm{kJ\ mol^{-1}}.$$

In these three dichloro and three dibromo complexes, the thermal stabilities decrease in the following orders,

$$\textit{trans}\text{-}[\mathrm{CoCl_2}(dl\text{-bn})_2]\mathrm{ClO_4} > \textit{trans}\text{-}[\mathrm{CoCl_2}(m\text{-bn})_2]\mathrm{ClO_4}$$
$$> \textit{trans}\text{-}[\mathrm{CoCl_2}(i\text{-bn})_2]\mathrm{ClO_4},$$
$$\textit{trans}\text{-}[\mathrm{CoBr_2}(dl\text{-bn})_2]\mathrm{ClO_4} > \textit{trans}\text{-}[\mathrm{CoBr_2}(m\text{-bn})_2]\mathrm{ClO_4}$$
$$> \textit{trans}\text{-}[\mathrm{CoBr_2}(i\text{-bn})_2]\mathrm{ClO_4}.$$

These orders coincide with those of the stability of tris(*l*-bn), tris(*m*-bn), and tris(*i*-bn) complexes in solution calculated from strain enthalpy.[3] The difference in the stabilities between bis(*dl*-bn) and bis(*m*-bn) or bis(*i*-bn) complexes can be understood from the fact that two methyl groups in the coordinated *dl*-bn (S, S-δ or R, R-λ) are equatorial,[2c] whereas one of two methyl groups in the *m*-bn (R, S-δ or R, S-λ) and *i*-bn (δ or λ) are in the axial position.

By using the following data,

$$dl\text{-ptn(l)} = dl\text{-ptn(aq)} \qquad \Delta H = -39.0\ \mathrm{kJ\ mol^{-1}},$$
$$dl\text{-ptn(l)} = dl\text{-ptn(g)} \qquad \Delta H = 37.0\ \mathrm{kJ\ mol^{-1}},$$
$$m\text{-ptn(l)} = m\text{-ptn(aq)} \qquad \Delta H = -39.6\ \mathrm{kJ\ mol^{-1}},$$
$$m\text{-ptn(l)} = m\text{-ptn(g)} \qquad \Delta H = 37.1\ \mathrm{kJ\ mol^{-1}},$$

the enthalpy changes for the following reactions are calculated:

$$\textit{trans}\text{-}[\mathrm{CoX_2}(\textit{dl}\text{-ptn})_2]\mathrm{X}\cdot 0.5\mathrm{H_2O(s)} + 2\textit{m}\text{-ptn(g)}$$

$$= \textit{trans}\text{-}[\mathrm{CoX_2}(\textit{m}\text{-ptn})_2]\mathrm{X}\cdot 0.5\mathrm{H_2O(s)} + 2\textit{dl}\text{-ptn(g)},$$

for $X = Cl^-$ $\Delta H = -20.5$ kJ mol^{-1},

for $X = Br^-$ $\Delta H = -8.8$ kJ mol^{-1}.

In these cases, the complexes containing the meso-form of ptn are thermally more stable than those containing the racemic form in contrast to the bis(bn) complexes. Such a difference will be ascribed to the difference in the conformation of the chelates, although the orientation of methyl groups is all equatorial in both complexes.[13]

The enthalpy changes for the substitution reaction of diamines are listed in Table 2.

Thermal Stability Differences between Dichloro Complex Chlorides and the Corresponding Dibromo Complex Bromides. Considering the following data,

$Cl^-(aq) = Cl^-(g)$ $\Delta H = -76.5$ kJ mol^{-1},[14]

$Br^-(aq) = Br^-(g)$ $\Delta H = -110.5$ kJ mol^{-1},[14]

the enthalpy changes for the following reactions,

$$\textit{trans}\text{-}[\mathrm{CoCl_2(AA)_2}]\mathrm{Cl}\cdot m\mathrm{HCl}\cdot n\mathrm{H_2O(s)} + (3+m)\mathrm{Br^-(g)}$$

$$= \textit{trans}\text{-}[\mathrm{CoBr_2(AA)_2}]\mathrm{Br}\cdot m\mathrm{HBr}\cdot n\mathrm{H_2O(s)} + (3+m)\mathrm{Cl^-(g)},$$

were calculated, which are summarized in Table 3.

These values correspond to the decrement of lattice energies of the solid complexes when chloride ions coordinated and/or those present as counter ions are replaced by bromide ions. It is shown that the dibromobis(diamine)cobalt(III) bromides are thermally less stable than the corresponding dichloro chlorides by about 35—70 kJ mol.$^{-1}$ Especially, a tendency seems to exist that, in the complexes containing 1,2-ethanediamine or the diamines with two methyl groups attached to the distant carbon atoms like ptn, the enthalpy increments in the replacement of Cl^- by Br^- are about 40 kJ mol.$^{-1}$ On the other hand, for the other complexes containing the diamines with two methyl groups at the adjacent carbon atoms like bn, the enthalpy increments are about 60 kJ mol.$^{-1}$

Thermal Stability Diagram of the Bis(en), Bis(pn) and Bis(tn) Complexes. The enthalpy change for the reaction of *trans*-$[CoCl_2en_2]Cl$ with an alkaline sodium sulfide solution is, as Table 1 shows, given as,

$$\textit{trans}\text{-}[\mathrm{CoCl_2en_2}]\mathrm{Cl(s)} + 3/2\ \mathrm{S^{2-}\ (aq)}$$

$$= 1/2\ \mathrm{Co_2S_3(s)} + 3\mathrm{Cl^-(aq)} + 2\mathrm{en(aq)}$$

$$\Delta H = -60.5 \text{ kJ mol}^{-1}. \tag{5}$$

Combining the value of Eq. 5 with that of Eq. 1 and the values[14] shown below,

$HCl(g) = H^+(aq) + Cl^-(aq)$ $\Delta H = -75.2$ kJ mol^{-1},

$H_2O(l) = H^+(aq) + OH^-(aq)$ $\Delta H = 55.9$ kJ mol^{-1},

$H_2O(l) = H_2O(g)$ $\Delta H = 44.0$ kJ mol^{-1},

the enthalpy change for the reaction,

$$\textit{trans}\text{-}[\mathrm{CoCl_2en_2}]\mathrm{Cl}\cdot\mathrm{HCl}\cdot 2\mathrm{H_2O(s)}$$

$$= \textit{trans}\text{-}[\mathrm{CoCl_2en_2}]\mathrm{Cl(s)} + \mathrm{HCl(g)} + 2\mathrm{H_2O(g)},$$

was calculated as $\Delta H = 162.2$ kJ mol^{-1}. Using this value, and taking account of the other data concerned, the enthalpy levels of some bis(en) and bis(pn) complexes are obtained, which are diagramatically shown in Fig. 1.

TABLE 3. ENTHALPY CHANGES, ΔH, FOR THE REACTION SUBSTITUTING Br^- FOR Cl^- IN COBALT (III) COMPLEXES

Complex	ΔH/kJ mol^{-1}
trans-$[CoX_2en_2]X\cdot HX\cdot 2H_2O$	40.4
trans-$[CoX_2en_2]X$	48.0
trans-$[CoX_2pn_2]X\cdot HX\cdot 2H_2O$	39.0
trans-$[CoX_2\ pn_2]X\cdot H_2O$	62.2
trans-$[CoX_2(l\text{-pn or }d\text{-pn})_2]X\cdot H_2O$	62.0
trans-$[CoX_2(dl\text{-bn})_2]ClO_4$	71.2
trans-$[CoX_2(m\text{-bn})_2]ClO_4$	67.3
trans-$[CoX_2(i\text{-bn})_2]ClO_4$	69.4
trans-$[CoX_2tn_2]X$	35.9
trans-$[CoX_2(dl\text{-ptn})_2]X\cdot 0.5H_2O$	34.9
trans-$[CoX_2(m\text{-ptn})_2]X\cdot 0.5H_2O$	46.6

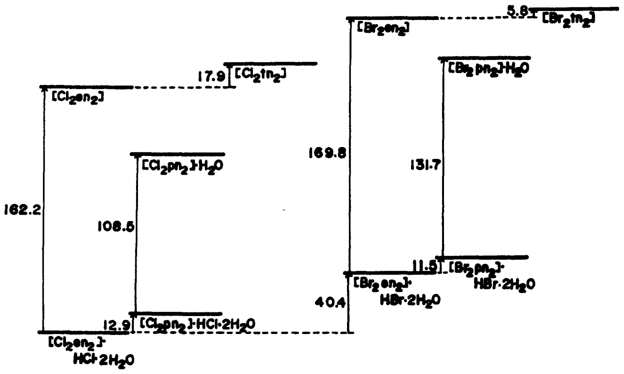

Fig. 1. Enthalpy level diagram for bis(en), bis(pn), and bis(tn) complexes. $[Cl_2en_2]\cdot HCl\cdot 2H_2O$ and $[Cl_2en_2]$ are abbreviations of *trans*-$[CoCl_2en_2]Cl\cdot HCl\cdot 2H_2O$ and *trans*-$[CoCl_2en_2]Cl$, respectively. Other abbreviations are similarly used. The numerals are expressed by the unit of kJ mol^{-1}.

Comparing the data in Table 2 with those in Table 3, the enthalpy changes for the substitution reaction of halide ions are considerably larger than those for the diamines. Such a tendency is obviously illustrated in Fig. 1 for each of the bis(en), bis(pn), and bis(tn) complexes. In summary, the thermal stability based on the lattice energy difference was found to be largely affected by the kind of halide ions rather than that of diamines.

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