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A Calorimetric Study on the Relative Thermal Stabilities of Some Cobalt(III)-Ammine Complexes in Solid Phase

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(Received May 20, 1983)

The enthalpy changes (ΔH) in the reaction of $[CoX_n(NH_3)_{6-n}]X_{3-n}$ type complexes with an alkaline sodium sulfide solution were calorimetrically measured at 25 °C, where X is Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-. The thermal stabilities were found to decrease in the following orders: in the hexaammine series, chloride>bromide>nitrate>iodide>perchlorate; in the pentaammine series, chloride>bromide>nitrate; and in the *trans*-tetraammine series, chloride>bromide and chloro>bromo complexes. In addition, in the tetraammine series, the possibility of trans-to-cis isomerization, which has actually been observed, was reasonably explained on the basis of the difference in lattice energies between *trans*- and *cis*-$[CoCl_2(NH_3)_4]Cl$.

In the previous paper, we measured calorimetrically the enthalpy changes in the reaction of solid $Ni(AA)_2X_2\cdot nH_2O$ (AA: *N,N*- or *N,N'*-diethylethylenediamine; X: Cl^-, Br^-, I^-, or NO_3^-; *n*: 0 or 2) with an aqueous potassium cyanide, and found that the thermal stabilities of the complexes decrease in the order, chloride>bromide>nitrate>iodide.[1] In addition, the enthalpy changes in the reaction of solid $[CoX_2(AA)_2]X$ type complexes (AA: diamine such as 1,2-ethanediamine; X: Cl^-, Br^-, or ClO_4^-) with an alkaline sodium sulfide solution were measured, and the differences in lattice energy among the above complexes were evaluated therefrom. Comparison of their lattice energies revealed that the thermal stabilities decrease in the order, chloride>bromide>perchlorate.[2] As a continuation of these calorimetric studies, the present study was undertaken to decide the order of the thermal stabilities among chloride, bromide, iodide, nitrate, and perchlorate in each series of the hexaammine-, pentaammine-, and tetraamminecobalt(III) complexes, and among the complexes of these three series when the anions involved are chloride, bromide and nitrate ions, respectively.

In $[CoX_2(en)_2]X$ type complexes (X=Cl^- or Br^-), the cis-to-trans isomerization was predicted to occur on the basis of the enthalpy measurement for trans- and cis-complexes, and the prediction was actually verified.[3] As for the corresponding ammine complexes, $[CoX_2(NH_3)_4]X$ (X:Cl^- or Br^-), however, no such calorimetric prediction has been made on the direction of isomerization (trans-to-cis or cis-to-trans). To solve this problem by the enthalpy measurement is the second purpose of this study.

Experimental

Preparation of Complexes. The following complexes were prepared by the literature methods: $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]Br_3$, $[Co(NH_3)_6](NO_3)_3$, $[Co(NH_3)_6]I_3$, $[Co(NH_3)_6](ClO_4)_3$,[4] $[CoCl(NH_3)_5]Cl_2$, $[CoCl(NH_3)_5]Br_2$,[5] $[CoBr(NH_3)_5]Br_2$, $[CoBr(NH_3)_5]Cl_2$,[6] $[Co(NO_3)(NH_3)_5](NO_3)_2$,[7] $[CoI(NH_3)_5]Cl_2$,[8] *trans*-$[CoCl_2(NH_3)_4]Cl$,[9] *cis*-$[CoCl_2(NH_3)_4]Cl$,[10] and *trans*-$[CoBr_2(NH_3)_4]Br$.[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 complex was accurately weighed and let react with 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 $[Co(NH_3)_6]X_3$ Complexes. The enthalpy changes (ΔH_{exp}) measured for the reaction of hexaammine cobalt(III) complexes with an alkaline sodium sulfide solution, *i.e.*, $[Co(NH_3)_6]X_3(s) + 3/2\ S^{2-}(aq) = 1/2\ Co_2S_3(s) + 6NH_3(aq) + 3X^-(aq)$ are summarized in Table 1. Combining these data with the values in the following changes,[12]

$$\left.\begin{aligned} &Cl^-(aq) = Cl^-(g) && \Delta H = -76.5\ \mathrm{kJ\ mol^{-1}} \\ &Br^-(aq) = Br^-(g) && \Delta H = -110.5\ \mathrm{kJ\ mol^{-1}} \\ &NO_3^-(aq) = NO_3^-(g) && \Delta H = -128.9\ \mathrm{kJ\ mol^{-1}} \\ &I^-(aq) = I^-(g) && \Delta H = -154.0\ \mathrm{kJ\ mol^{-1}} \\ &ClO_4^-(aq) = ClO_4^-(g) && \Delta H = -217.6\ \mathrm{kJ\ mol^{-1}} \end{aligned}\right\}, \quad (1)$$

the enthalpy changes (ΔH_{rel}) for the following reactions, $[Co(NH_3)_6]Cl_3(s)+3X^-(g)=[Co(NH_3)_6]X_3(s)+3Cl^-(g)$, were calculated as below:

$$\begin{aligned} &\text{for } X^- = Br^- && \Delta H_{rel} = 82.6\ \mathrm{kJ\ mol^{-1}}, \\ &\text{for } X^- = NO_3^- && \Delta H_{rel} = 125.2\ \mathrm{kJ\ mol^{-1}}, \\ &\text{for } X^- = I^- && \Delta H_{rel} = 210.0\ \mathrm{kJ\ mol^{-1}}, \\ &\text{for } X^- = ClO_4^- && \Delta H_{rel} = 377.5\ \mathrm{kJ\ mol^{-1}}. \end{aligned}$$

These values correspond to the decreases of lattice energies of the solid complexes which give the magnitudes of instabilities of the bromide, nitrate, iodide, and perchlorate relative to that of the chloride as a standard. The enthalpy levels for the hexaammine complexes are diagrammatically shown in Fig. 1. The numeral attached to each level is the value obtained above. Inspection of the figure reveals that, in this series of complexes, the thermal stability decreases in

Table 1. Enthalpy changes, ΔH_{exp}, for the reaction of cobalt(III)-ammine complexes $[CoX_n(NH_3)_{6-n}]X_{3-n}$ with sodium sulfide solution ($\mathrm{kJ\ mol^{-1}}$)

X	$[Co(NH_3)_6]X_3$	$[CoX(NH_3)_5]X_2$	$[CoX_2(NH_3)_4]X$	
			trans	*cis*
Cl^-	29.5	12.2	−70.8	−56.2
Br^-	48.9	23.7	−215	
NO_3^-	61.5	29.6		
I^-	52.0			
ClO_4^-	75.3			

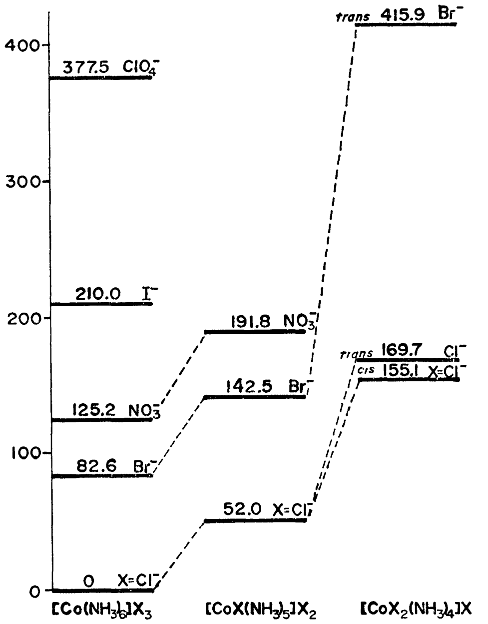

Fig. 1. Enthalpy level diagram for $[Co(NH_3)_6]X_3$, $[CoX(NH_3)_5]X_2$, and $[CoX_2(NH_3)_4]X$, where X is Cl^-, Br^-, NO_3^-, I^-, or ClO_4^-. The numerals are in kJ mol^{-1}.

the order, chloride > bromide > nitrate > iodide > perchlorate.

Thermal Stability of [CoX(NH$_3$)$_5$]X$_2$ Complexes. Combining the values of the enthalpy changes measured for the reaction of the pentaammine series of complexes (Table 1) with the values (1) concerned, the enthalpy changes (ΔH_{rel}) for substituting bromide and nitrate ions for chloride ions in chloropentaamminecobalt(III) chloride were calculated as below:

$$[CoCl(NH_3)_5]Cl_2(s) + 3X^-(g)$$
$$= [CoX(NH_3)_5]X_2(s) + 3Cl^-\ (g),$$
$$\text{for } X^- = Br^- \qquad \Delta H_{rel} = 90.5\ \text{kJ mol}^{-1},$$
$$\text{for } X^- = NO_3^- \qquad \Delta H_{rel} = 139.8\ \text{kJ mol}^{-1}.$$

In the series of pentaammine complexes in which both the ion coordinated and the counter anions are the same, it is evident that the thermal stability decreases in the order, chloride > bromide > nitrate. The situation is parallel to the case of the hexaammine series (Fig. 1).

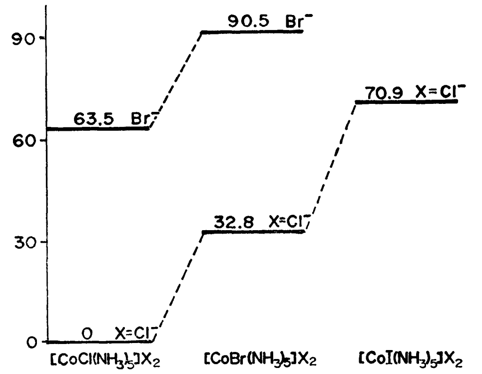

Fig. 2. Enthalpy level diagram for $[CoCl(NH_3)_5]X_2$, $[CoBr(NH_3)_5]X_2$ ($X = Cl^-$ or Br^-) and $[CoI(NH_3)_5]Cl_2$. The numerals are in kJ mol^{-1}.

On the other hand, in the complexes where the counter halide ion is varied from Cl^- to Br^- without changing the coordinated ion, and where the coordinated ion is varied from Cl^- to Br^- and then to I^- without changing the counter ion, the enthalpy changes (ΔH_{exp}) measured and those (ΔH_{rel}) evaluated from them for successive substitution of halide anions inside and outside the coordination sphere are summarized in Table 2. The enthalpy levels of these pentaammine complexes are illustrated in Fig. 2. As seen in Table 2 and Fig. 2, if the counter ion is varied, the thermal stability of the bromides is less stable than that of the corresponding chlorides in both chloro- and bromo-complexes. The enthalpy changes (ΔH_{rel}) for substituting Br^- and I^- for Cl^- coordinated in the series of complex chlorides suggest that the thermal stabilities decrease in the order, chloro- > bromo- > iodo-complexes. And the enthalpy change for substituting Br^- for Cl^- coordinated in the bromide indicates the stability of the bromo complex to be lower than that of the chloro complex. This order coincides with that of the decrease of ligand field strength of halide ions.

It should be, in addition, noted from Fig. 2 that the enthalpy change for substituting Br^- for Cl^- per one mole of halide ion is about 30 kJ regardless of whether the halide ion is inside or outside the coor-

TABLE 2. ENTHALPY CHANGES, ΔH_{exp}, FOR THE REACTION WITH SODIUM SULFIDE SOLUTION AND ENTHALPY CHANGES, ΔH_{rel}, FOR SUBSTITUTION REACTION OF HALIDE ION INSIDE OR OUTSIDE THE COORDINATION SPHERE IN SERIES OF PENTAAMMINECOBALT(III) COMPLEXES (kJ mol^{-1})

	Chloro series		Bromo series		
Chloride series	$[CoCl(NH_3)_5]Cl_2$		$[CoBr(NH_3)_5]Cl_2$		$[CoI(NH_3)_5]Cl_2$
ΔH_{exp}	12.2		13.4		18.8
ΔH_{rel}	0	⟶	32.8	⟶	70.9
	0		0		
ΔH_{rel}	↓		↓		
	63.5		57.7		
Bromide series	$[CoCl(NH_3)_5]Br_2$		$[CoBr(NH_3)_5]Br_2$		
ΔH_{exp}	16.7		23.7		
ΔH_{rel}	0	⟶	27.0		

dination sphere.

Comparison of Thermal Stability among Hexaammine, Pentaammine, and Tetraammine Complexes. By combining the enthalpy changes in Table 1 with the following value,[12)]

$$\mathrm{NH_3(aq)} = \mathrm{NH_3(g)} \qquad \Delta H = 34.7\ \mathrm{kJ\ mol^{-1}},$$

the enthalpy changes (ΔH_{rel}) for substituting chloride ion for ammonia in hexaamminecobalt(III) chloride to form chloropentaammine and dichlorotetraammine chlorides were obtained as follows:

$$[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3(s)} = [\mathrm{CoCl(NH_3)_5}]\mathrm{Cl_2(s)} + \mathrm{NH_3(g)}$$
$$\Delta H_{\mathrm{rel}} = 52.0\ \mathrm{kJ\ mol^{-1}},$$

$$[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3(s)} = \textit{trans}\text{-}[\mathrm{CoCl_2(NH_3)_4}]\mathrm{Cl(s)} + 2\mathrm{NH_3(g)}$$
$$\Delta H_{\mathrm{rel}} = 169.7\ \mathrm{kJ\ mol^{-1}},$$

$$[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3(s)} = \textit{cis}\text{-}[\mathrm{CoCl_2(NH_3)_4}]\mathrm{Cl(s)} + 2\mathrm{NH_3(g)}$$
$$\Delta H_{\mathrm{rel}} = 155.1\ \mathrm{kJ\ mol^{-1}}.$$

The enthalpy changes (ΔH_{rel}) for substituting bromide ion for ammonia in hexaamminecobalt(III) bromide and those for substituting nitrate ion in the corresponding nitrate were also obtained similarly as below,

$$[\mathrm{Co(NH_3)_6}]\mathrm{Br_3(s)} = [\mathrm{CoBr(NH_3)_5}]\mathrm{Br_2(s)} + \mathrm{NH_3(g)}$$
$$\Delta H_{\mathrm{rel}} = 59.9\ \mathrm{kJ\ mol^{-1}},$$

$$[\mathrm{Co(NH_3)_6}](\mathrm{NO_3})_3\mathrm{(s)}$$
$$= [\mathrm{Co(NO_3)(NH_3)_5}](\mathrm{NO_3})_2\mathrm{(s)} + \mathrm{NH_3(g)}$$
$$\Delta H_{\mathrm{rel}} = 66.6\ \mathrm{kJ\ mol^{-1}}.$$

In order to illustrate the thermal stabilities of all the cobalt(III) ammine complexes, the enthalpy levels for pentaammine and tetraammine complexes are also shown in Fig. 1. The numeral designated at each enthalpy level reflects the difference of their lattice energies. Thus, the figure shows that the thermal stabilities decrease in the order,

$$[\mathrm{Co(NH_3)_6}]\mathrm{X_3} > [\mathrm{CoX(NH_3)_5}]\mathrm{X_2} >$$
$$\textit{trans-}\text{ or }\textit{cis-}[\mathrm{CoX_2(NH_3)_4}]\mathrm{X},$$

where $\mathrm{X{=}Cl^-}$ or $\mathrm{Br^-}$.

Difference of Thermal Stability between trans- *and* cis-*[CoCl$_2$(NH$_3$)$_4$]Cl complexes and Thermodynamic Possibility of Isomerization.* The occurrence of the partial trans-to-cis isomerization of $[\mathrm{CoCl_2(NH_3)_4}]\mathrm{Cl}$ has already been reported.[13)] However, there have been no thermodynamical data to support this observation. Therefore, the enthalpy change of the trans-to-cis isomerization was estimated as below as shown in Table 1 and Fig. 1.

$$\textit{trans}\text{-}[\mathrm{CoCl_2(NH_3)_4}]\mathrm{Cl(s)} = \textit{cis}\text{-}[\mathrm{CoCl_2(NH_3)_4}]\mathrm{Cl(s)}$$
$$\Delta H = -14.6\ \mathrm{kJ\ mol^{-1}}$$

Statistically, the entropy change of the isomerization is evaluated as[3)]

$$\Delta S = 11.5\ \mathrm{J\ mol^{-1}\ K^{-1}}.$$

The free energy change is, therefore, calculated as

$$\Delta G^\circ = -28.0\ \mathrm{kJ\ mol^{-1}}$$

These data are consistent with the fact that the trans-to-cis isomerization takes place in $[\mathrm{CoCl_2(NH_3)_4}]\mathrm{Cl}$.

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