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A CALORIMETRIC STUDY ON THE RELATIVE THERMAL STABILITIES OF SOME COBALT(III)-TRIS(DIAMINE) AND -BIS(TRIAMINE) COMPLEXES IN THE SOLID PHASE

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ABSTRACT

The enthalpy changes for the reaction of $[Co(AA)_3]X_3$ and $[Co(dien)_2]X_3$ type complexes with an alkaline sodium sulfide solution were calorimetrically measured at 25°C, where AA is the diamine such as en, pn, tn, bpy or phen and X is Cl, Br, NO_3, I or ClO_4. The thermal stabilities were found to decrease in the following orders: chloride > bromide > nitrate > iodide > perchlorate; aliphatic diamine > aromatic diamine complexes; five-membered chelate > six-membered chelate compounds; and tris(diamine) > bis(triamine) complexes.

INTRODUCTION

In the previous paper (ref.1), the enthalpy changes were calorimetrically measured for the reaction of some solid cobalt(III)-ammine complexes, $[CoX_n(NH_3)_{6-n}]X_{3-n}$, with an alkaline solution of sodium sulfide, and it was found that the thermal stabilities of the complexes decrease in the following orders; chloride > bromide > nitrate > iodide > perchlorate in each series of the same type complexes; chloro > bromo > nitrato complexes in the series of $[CoX(NH_3)_5]X_2$; and $[Co(NH_3)_6]X_3 > [CoX(NH_3)_5]X_2 > [CoX_2(NH_3)_4]X$ (X=Cl etc.). When six molecules of unidentate ligand are replaced by three bidentate ligands or two terdentate ligands, what change appears in the thermal stability? The present study was undertaken to decide calorimetrically the order of the thermal stabilities among the tris(diamine)cobalt(III) complexes and the bis(triamine) complex and to compare the thermal stabilities of them with those of the hexaammine complexes. As the diamines, 1,2-ethanediamine (en), 1,2-propanediamine (pn), 1,3-propanediamine (tn), 2,2'-bipyridyl (bpy) and 1,10-phenanethroline (phen) were selected, and bis(2-aminoethyl)amine (dien) was used as the triamine.

EXPERIMENTAL

Preparation of complexes

The following complexes were prepared by the literature methods slightly modified: $[Co(en)_3]X_3$ (X=Cl, Br) (ref.2), $[Co(pn)_3]X_3$ (X=Cl, Br, I, NO_3) (ref.3), $[Co(tn)_3]X_3$ (X=Cl, Br) (ref.4), $[Co(bpy)_3]X_3$ (X=Cl, Br, NO_3, ClO_4), $[Co(phen)_3]X_3$ (X=Cl, Br, NO_3, ClO_4) (ref.5) and $[Co(dien)_2]X_3$ (X=Cl, Br, I, NO_3) (ref.6).

Calorimetric measurements

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

RESULTS AND DISCUSSION

Thermal stability of $[Co(pn)_3]X_3$ complexes

The enthalpy changes (ΔH exp) measured for the reactions of tris(diamine)- and bis(triamine)cobalt(III) complexes with an alkaline sodium sulfide solution are summarized in Table 1. For comparison, the corresponding enthalpy changes for hexaamminecobalt(III) complexes are also included in the table.

Above all, combining the values of the enthalpy changes for the reactions,

$$[Co(pn)_3]X_3(s) + 3/2S^{2-}(aq) = 1/2Co_2S_3(s) + 3pn(aq) + 3X^-(aq),$$

where X^- is Cl^-, Br^-, NO_3^- or I^-, with the values in the following changes (ref. 7),

$$\begin{aligned} Cl^-(aq) &= Cl^-(g) & \Delta H &= -76.5\ kJ\ mol^{-1} \\ Br^-(aq) &= Br^-(g) & \Delta H &= -110.5\ kJ\ mol^{-1} \\ NO_3^-(aq) &= NO_3^-(g) & \Delta H &= -128.9\ kJ\ mol^{-1} \\ I^-(aq) &= I^-(g) & \Delta H &= -154.0\ kJ\ mol^{-1} \end{aligned} \qquad (1)$$

the enthalpy changes for the reactions,

$$[Co(pn)_3]Cl_3(s) + 3X^-(g) = [Co(pn)_3]X_3(s) + 3Cl^-(g),$$

were calculated as below:

TABLE 1

Enthalpy changes, ΔH exp, for the reaction of cobalt(III) complexes, $[Co(NH_3)_6]X_3$, $[Co(AA)_3]X_3$ and $[Co(dien)_2]X_3$, with sodium sulfide solution (/kJ mol^{-1}).

X	AA	$6NH_3$	3en	3pn	3tn	3bpy	3phen	2dien
Cl		29.5	27.3	24.0	-10.6	16.4	-43.5	37.8
Br		48.9	46.2	39.5	-27.3	20.6	-33.7	60.1
NO_3		61.5		60.6		-38.3	-41.0	65.8
I		52.0		73.2				80.6
ClO_4		75.3				-45.0		

for $X^- = Br^-$ $\Delta H = 86.5$ kJ mol^{-1}
for $X^- = NO_3^-$ $\Delta H = 120.6$ kJ mol^{-1}
for $X^- = I^-$ $\Delta H = 183.3$ kJ mol^{-1}.

These values correspond to the decreases in lattice energies of the solid complexes which show the magnitudes of instabilities of the bromide, nitrate and iodide relative to that of the chloride as the standard. The enthalpy levels for $[Co(pn)_3]X_3$ complexes are diagrammatically shown in Fig. 1, together with those for other tris(diamine)- and bis(triamine)cobalt(III) complexes and for $[Co(NH_3)_6]X_3$ complexes. The numerals attached to each level are the values obtained above. Inspection of the figure reveals that the thermal stability decreases in the order, chloride > bromide > nitrate > iodide in the pn complexes.

Thermal stability of $[Co(AA)_3]Cl_3$ and $[Co(dien)_2]Cl_3$ complexes

In order to find the relative thermal stabilities of various $[Co(AA)_3]Cl_3$ and $[Co(dien)_2]Cl_3$ complexes in the solid state, where AA is en, pn, tn, bpy or

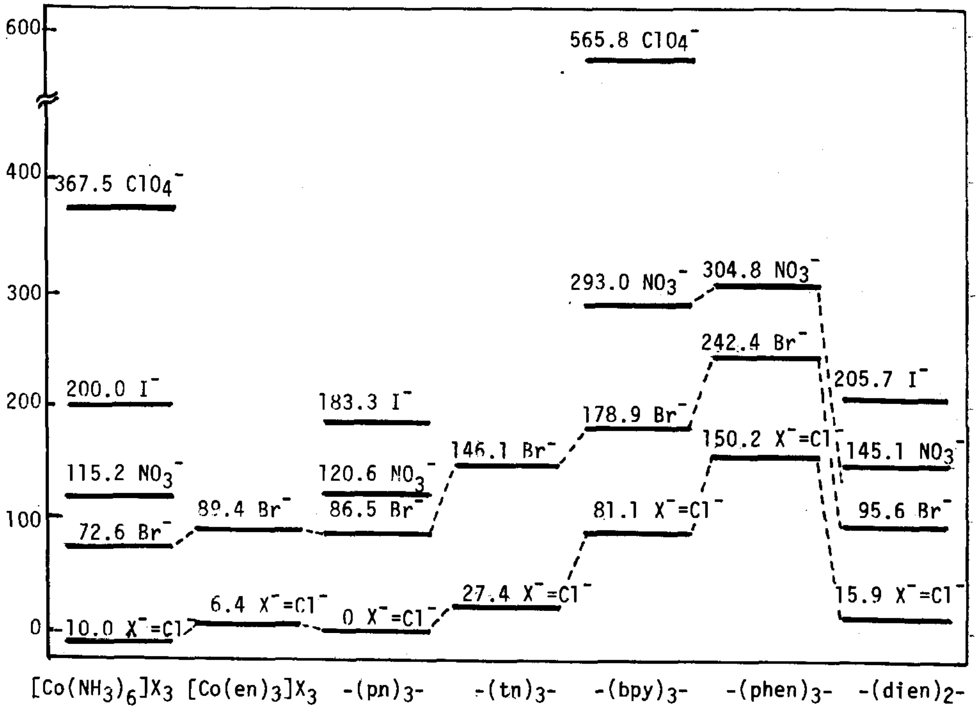

Fig. 1. Enthalpy level diagrams for $[Co(NH_3)_6]X_3$, $[Co(AA)_3]X_3$ and $[Co(dien)_2]X_3$, where X is Cl, Br, NO_3, I or ClO_4 and AA is en, pn, tn, bpy or phen. The numerals are in unit of kJ mol^{-1}.

phen, the heats of dissolution of diamines and triamine into an alkaline sodium sulfide solution were measured with the calorimeter, and their heats of vaporization were calculated from the boiling points and Trouton's constant. The heats of dissolution were -30.4 (en), -33.4 (pn), -34.4 (tn), 4.5 (bpy), 11.0 (phen) and -44.7 kJ mol^{-1} (dien), and the heats of vaporization were 34.3 (en), 34.5 (pn), 35.9 (tn), 48.0 (bpy), 51.3 (phen) and 42.3 kJ mol^{-1} (dien). From these values, the enthalpy changes of the respective diamine and triamine in the change to the gaseous state from the aqueous solution were calculated.

Combining these values with the values of the enthalpy changes measured for the reactions of the complexes with Na_2S (Table 1), the enthalpy changes for the substitution reactions,

$$[Co(pn)_3]Cl_3(s) + 3AA(g) \text{ or } 2dien(g) = [Co(AA)_3]Cl_3(s) \text{ or } [Co(dien)_2]Cl_3(s) + 3pn(g),$$

were calculated as follows:

$$\begin{array}{lll} \text{for AA = en} & \Delta H = 6.4 \text{ kJ mol}^{-1} \\ \text{for AA = tn} & \Delta H = 27.4 \text{ kJ mol}^{-1} \\ \text{for AA = bpy} & \Delta H = 81.1 \text{ kJ mol}^{-1} \\ \text{for AA = phen} & \Delta H = 150.0 \text{ kJ mol}^{-1} \\ \text{for dien} & \Delta H = 15.9 \text{ kJ mol}^{-1} \end{array} \qquad (2)$$

These data suggest that the complexes containing these diamines or triamine are thermally unstable by the respective enthalpy changes described above relative to $[Co(pn)_3]Cl_3$ in the solid state.

In the same manner as that presented in the foregoing sections, by using the data of the heat of reactions measured (Table 1) and the values of the enthalpy change of anions (1) together with that concerning the perchlorate ion, $ClO_4^-(aq) = ClO_4^-(g)$, $\Delta H = -217.6$ kJ mol^{-1} (ref.7), the enthalpy changes for the substitution reactions,

$$[Co(AA)_3]Cl_3(s) \text{ or } [Co(dien)_2]Cl_3(s) + 3X^-(g) = [Co(AA)_3]X_3(s) \text{ or } [Co(dien)_2]X_3(s) + 3Cl^-(g),$$

were calculated, where AA is en, tn, bpy or phen and X^- is Br^-, NO_3^-, I^- or ClO_4^-.

Combining these values with the enthalpy changes, (2), the enthalpy changes for the following reactions (substituting various diamines or triamine for pn, and/or substituting several counter anions for Cl^-) were obtained:

$$[Co(pn)_3]Cl_3(s) + 3AA(g), 2dien(g) \text{ or } 3X^-(g) = [Co(AA)_3]X_3(s) \text{ or } [Co(dien)_2]X_3(s) + 3pn(g) \text{ or } 3Cl^-(g).$$

These values correspond to the differences in the lattice energy between $[Co(AA)_3]X_3(s)$ or $[Co(dien)_2]X_3(s)$ and $[Co(pn)_3]Cl_3(s)$, and give the relative thermal stabilities of the complexes.

Summary on the thermal stabilities among the complexes

The enthalpy level diagrams illustrated in Fig. 1 tell us the following several valuable informations.

1) Effect of anion substitution. The thermal stability decreases in the order, chloride >bromide >nitrate >iodide >perchlorate in each series of the respective complex types. The order is parallel to the reverse order of the anionic radii Cl^-(1.81 A) <Br^-(1.96 A) <I^-(2.20 A) <ClO_4^-(2.36 A) except for NO_3^-(1.89 A) (ref.8) irrespective of the kind of the complex types. The parallel relationship is readily recognized from the fact that the Coulombic interaction between the complex cations and the counter anions becomes smaller because the electrical density on the surface of the anions decreases with the increase of the radii.

2) The difference between aliphatic and aromatic diamines. The complexes containing the aromatic diamines (bpy and phen) are thermally less stable than those containing the aliphatic diamines (en , pn and tn). This may be due to the larger steric hindrance of the former diamines in the complex formation than that of the latter, because the former diamines have the larger substituents of aromatic rings.

3) The difference between bpy and phen. The bpy complexes are more stable than the corresponding phen complexes. It may be reasonably explained by the difference in the structures in which bpy molecule is relatively flexible in the bond between two pyridine rings, whereas the skeleton of phen molecule is fixed by the benzene ring intervening in two pyridine rings, and so the strain enthalpy in the complex formation is a little smaller in the former than in the latter.

4) The number of members in chelate ring. The complexes containing five-membered chelate rings such as en or pn are more stable than those having six-membered rings as tn. It may be attributable to a little larger strain in the complex formation of the latter chelate than in that of the former. One of the origins of the larger strain in the latter is easily understood from the fact that the bond angle N-Co-N in tn complexes is about 95°, while that in en and pn complexes is < 90° and near 90° than that in tn complexes (ref.9).

5) The difference among uni-, bi- and terdentate ligands. In the discussion of the above items 1-4), the stabilities were compared among the same series of complexes, in which the ligand-environments around the cobalt(III) ion are essentially similar to each other. Therefore, it may be expected that the stabilities of the complexes are more dominantly influenced by the enthalpy change (namely, the lattice energy) than the entropy change for complex formation; the contribution of entropy change can be neglected. On the other hand, the same is not true for the different series of complexes because the entropy changes for

complex formation are appreciably different among uni-, bi- and terdentate ligands.

In the present study, however, the thermal stability was found to decrease in the order of the complexes of unidentate (NH_3) > bidentate (en, pn) > terdentate (dien). This is reverse to the thermodynamic stability order. Furthermore, the basicity of amines becomes larger in the order of primary < secondary < tertiary (ref.10), and so the coordination ability may be larger in the order, NH_3 < en, pn < dien in complex formation. Nevertheless, the thermal stability was reverse. It may be due to the fact that the steric strain becomes larger with the increased n-membered chelate ring.

REFERENCES

1 R. Tsuchiya, A. Uehara and T. Nakayama, Bull. Chem. Soc. Jpn., 56 (1983) 3284-3286.
2 W.C. Fernelius (Eds.), "Inorg. Synth.," Vol. II, 1952, 221-222.
3 A. Wold and J.K. Ruff (Eds.), "Inorg. Synth.," Vol. XIV, 1973, 57-60.
4 J.C. Bailar, Jr. and B. Work, J. Am. Chem. Soc., 68 (1946) 232-235.
5 N. Maki, Bull. Chem. Soc. Jpn., 42 (1969) 2275-2281.
6 Y. Yoshikawa and K. Yamasaki, Bull. Chem. Soc. Jpn., 45 (1972) 179-184.
7 F.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," U.S. Government Printing Office, Washington, D.C. 1952.
8 V.M. Goldschmidt, Ber., 60 (1927) 1263; L. Pauling, J. Am. Chem. Soc., 49 (1927) 765.
9 J.R. Gollogly and C.J. Hawkins, Inorg. Chem., 8 (1969) 1168-1173.
10 F. Basolo and R.K. Murmann, J. Am. Chem. Soc., 74 (1952) 5243-5246; 76 (1954) 211-214; H.B. Jonassen, R.B. Leblanc, A.W. Meinborn and R.M. Rogan, J. Am. Chem. Soc., 72 (1950) 2430-2433.