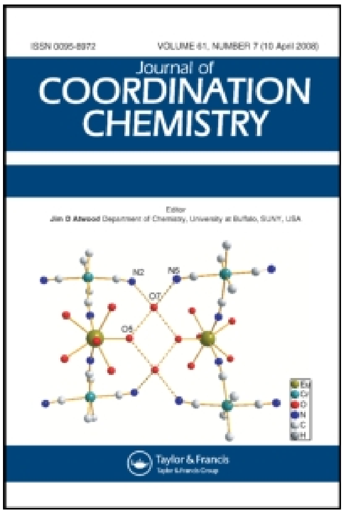

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FORMATION OF THE INTERMEDIATE, AQUOHYDROXOBIS (ETHYLENEDIAMINE)COBALT(III) COMPLEX, IN THE PREPARATION OF *CIS*-BROMOAMMINEBIS (ETHYLENEDIAMINE)COBALT(III) BROMIDE BY THE REACTION OF BIS[BIS(ETHYLENEDIAMINE)COBALT(III)-μ-DIHYDROXO]DIAQUOCOBALT(II) SULFATE WITH AMMONIUM BROMIDE IN WATER

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The production of *cis*-$[CoBr(NH_3)(en)_2]Br_2$ by reaction of $[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2](SO_4)_2$ with ammonium bromide in water was investigated. The reaction seems to proceed through the intermediate, $[Co(H_2O)(OH)(en)_2]^{2+}$, and then convert to the product, *cis*-$[CoBr(NH_3)(en)_2]^{2+}$. This is supported by the observation that the absorption spectrum of the reaction solution immediately after the disappearance of the starting complex was different from that of *cis*-$[CoBr(NH_3)(en)_2]^{2+}$ but was quite similar to that of $[Co(H_2O)(OH)(en)_2]^{2+}$. In order to confirm this reaction pathway, *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$ was prepared and reacted with ammonium bromide producing the expected complex, *cis*-$[CoBr(NH_3)(en)_2]Br_2$.

Keywords: Cobalt; ethylenediamine; ammonium bromide; reaction mechanisms; intermediate

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INTRODUCTION

The octahedral cobalt complex, *cis*-$[CoBr(NH_3)(en)_2]Br_2$, can be prepared by several methods.[1–4] The complex could be resolved into its enantiomers,[5,6] and the absolute structures of the enantiomers have been determined.[7,8]

One of the methods to prepare the complex is reaction of $[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2](SO_4)_2$ with ammonium bromide in water.[3,4] Our interest in this reaction system stems from our observation[9] that this reaction can spontaneously generate chiral asymmetry, *i.e.*, preferentially produce an excess of one enantiomer, either Λ or Δ. When the reaction was carried out in the presence of a small amount of crystals of one enantiomer, the same enantiomer was preferentially produced. The chiral asymmetry generation was thus thought to occur by chiral autocatalysis involving the solid phase, and the mechanism has been investigated.[10,11]

In the present study, reaction of $[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2](SO_4)_2$ with ammonium bromide in water was investigated in more detail. We found that the intermediate, $[Co(H_2O)(OH)(en)_2]^{2+}$, was produced during the reaction and then converted into *cis*-$[CoBr(NH_3)(en)_2]Br_2$. In order to confirm this mechanism, we prepared *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$, reacted it with ammonium bromide and found that the expected product, *cis*-$[CoBr(NH_3)(en)_2]Br_2$, formed.

EXPERIMENTAL

Materials and Instruments

The complexes, $[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2](SO_4)_2$ and *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$ were prepared by published methods.[12,13] Ammonium bromide (A. C. S. reagent) was purchased from Aldrich Chemical Co., Inc. Distilled water was used throughout the experiments. Absorption spectra were recorded on a Hewlett Packard 8452A spectrophotometer.

Isolation and Determination of the Intermediate and Resulting Complexes

After stirring the reaction mixture for a certain time, it was poured into a large amount of ice to stop the reaction. This solution was then passed through an ion-exchange resin column (Sephadex SP C-25) to separate the complexes, $[Co(H_2O)(OH)(en)_2]^{2+}$ and *cis*-$[CoBr(NH_3)(en)_2]^{2+}$, using ammonium bromide aqueous solution as eluent. Intensity of the absorption at 512 nm from $[Co(H_2O)(OH)(en)_2]^{2+}$ and the absorption at 542 nm from *cis*-$[CoBr(NH_3)(en)_2]^{2+}$ were measured to calculate the concentrations. Yields were calculated from the volume and concentrations of the eluate.

Isolation of Pure Crystalline *cis*-$[CoBr(NH_3)(en)_2]Br_2$ from the Reaction Mixture

After the reaction of *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$ with ammonium bromide was complete, the mixture was kept at 0°C for 1 h. The solid material thus obtained was filtered off. It was dissolved in 5.0 mL of 5.0% hydrobromic acid at 90°C, and recrystallized letting the solution stand for 1 h at 0°C. It was then filtered off and washed with methanol and diethyl ether and air dried for 1 h.

RESULTS AND DISCUSSION

When the mixture of $[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2](SO_4)_2$ and ammonium bromide in water was stirred at room temperature and then stirred for 5 min in a 50°C water bath, the octahedral cobalt complex, *cis*-$[CoBr(NH_3)(en)_2]Br_2$, was produced. Almost all starting complex disappeared after 1 min stirring. The absorption spectrum of the reaction solution at this time, however, was different from that of *cis*-$[CoBr(NH_3)(en)_2]Br_2$ as shown in Figure 1. The spectrum suggested that the main product in the reaction mixture at this time was $[Co(H_2O)(OH)(en)_2]^{2+}$.[14]

The results indicate that *cis*-$[CoBr(NH_3)(en)_2]Br_2$ is not directly synthesized by the reaction. Instead, the intermediate complex, $[Co(H_2O)(OH)(en)_2]^{2+}$, is produced, which then converts to *cis*-$[CoBr(NH_3)(en)_2]^{2+}$.

During the reaction, the change in the amount of starting complex, the amounts of *cis*-$[CoBr(NH_3)(en)_2]^{2+}$ and $[Co(H_2O)(OH)(en)_2]^{2+}$, and the change in the temperature of the reaction system are shown in Figure 2. The temperature initially drops because dissolution of ammonium bromide is endothermic. The conversion to the intermediate was quite rapid and nearly complete in one minute. The final product, *cis*-$[CoBr(NH_3)(en)_2]^{2+}$, was inhibited when the temperature of the reaction system was below 20°C.

In order to confirm this sequence, reaction of *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$ with ammonium bromide was carried out in water giving the expected complex, *cis*-$[CoBr(NH_3)(en)_2]Br_2$. The reaction was conducted under different conditions with the corresponding yields of *cis*-$[CoBr(NH_3)(en)_2]Br_2$ shown in Table I.

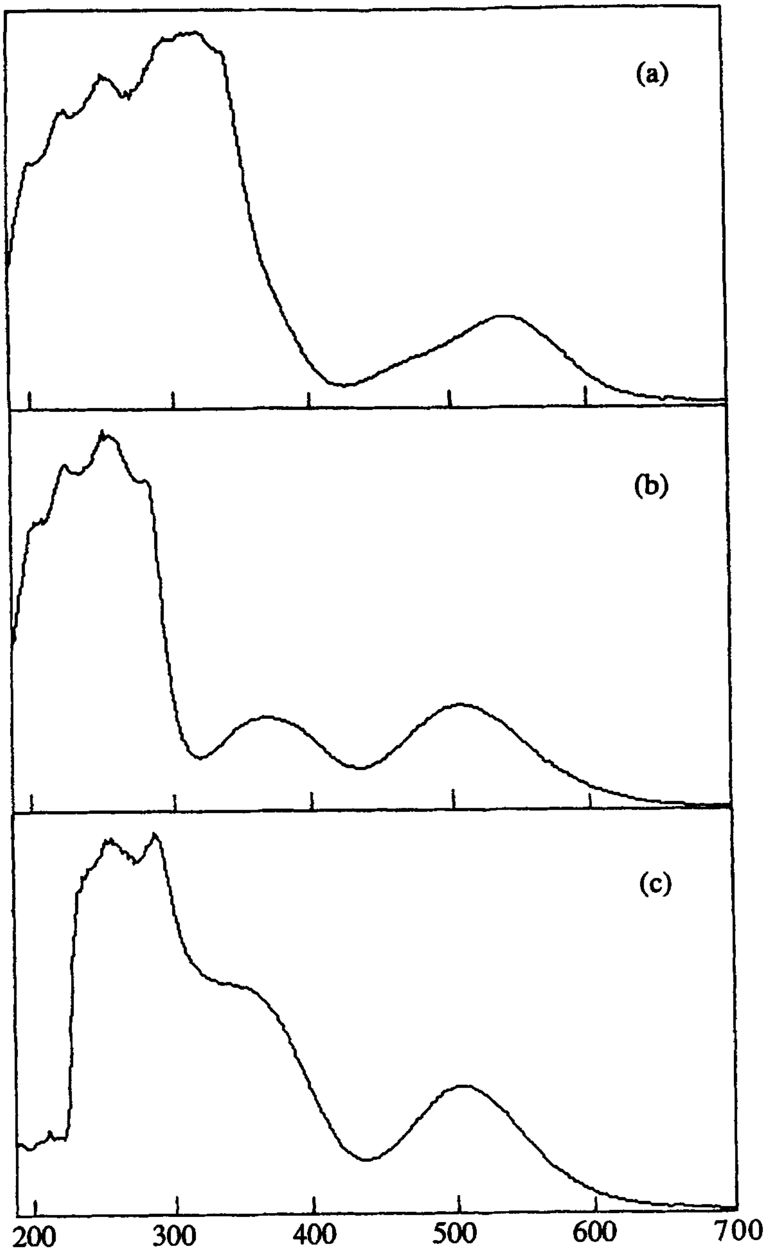

FIGURE 1 Absorption spectra of (a): *cis*-$[CoBr(NH_3)(en)_2]Br_2$; (b): *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$; (c): reaction solution after stirring for 1 min.

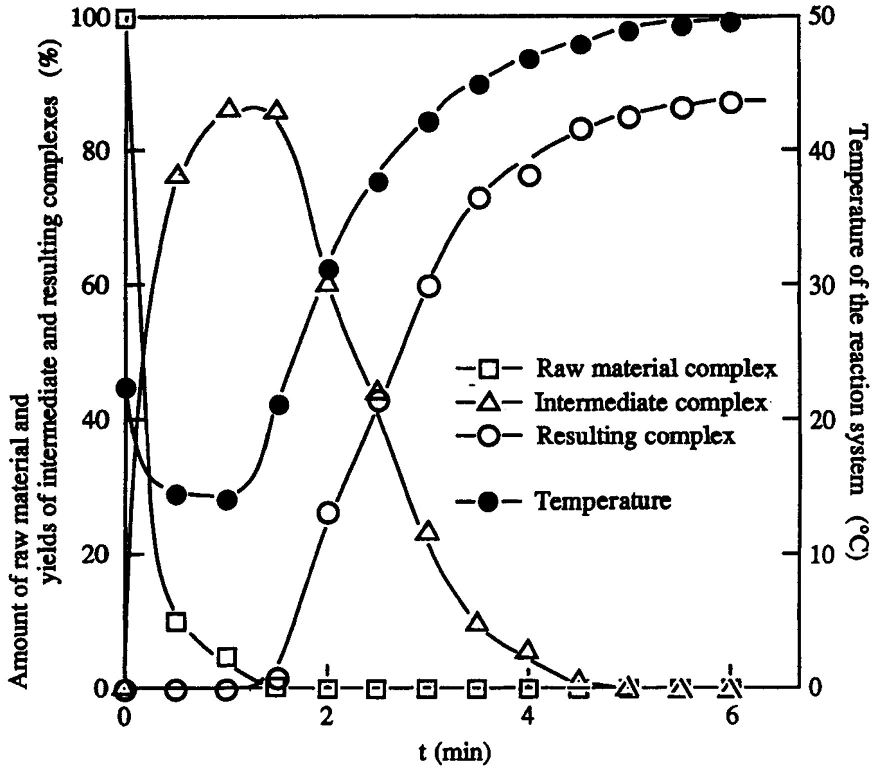

FIGURE 2 Changes of the amount of raw material complex, the yields of the intermediate and resulting complex, and the temperature of the reaction system as a function of time.

TABLE I Yields of *cis*-$[CoBr(NH_3)(en)_2]Br_2$ obtained by the reaction of *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$ with ammonium bromide in aqueous media

Run	*Time* (h)	*Water* (mL)	*cis*-$[Co(H_2O)(OH)(en)_2]Br_2$ (mol)	*Ammonium bromide* (mol)	*Yield* (%)
1	24	5.0	5.00×10^{-4}	2.50×10^{-3}	0.0
2	24	5.0	5.00×10^{-4}	1.25×10^{-2}	0.0
3	24	5.0	5.00×10^{-4}	2.00×10^{-2}	0.0
4	24	5.0	5.00×10^{-4}	2.50×10^{-2}	29.9
5	24	5.0	5.00×10^{-4}	3.75×10^{-2}	70.5
6	24	5.0	5.00×10^{-4}	5.00×10^{-2}	76.1
7	24	5.0	2.50×10^{-3}	2.50×10^{-3}	0.0
8	24	5.0	2.50×10^{-3}	1.25×10^{-2}	0.0
9	24	5.0	2.50×10^{-3}	2.00×10^{-2}	0.0
10	24	5.0	2.50×10^{-3}	2.50×10^{-2}	0.0
11	24	5.0	2.50×10^{-3}	3.75×10^{-2}	56.7
12	24	5.0	2.50×10^{-3}	5.00×10^{-2}	55.3
13	72	5.0	2.50×10^{-3}	3.75×10^{-2}	83.6
14	72	5.0	2.50×10^{-3}	5.00×10^{-2}	89.3

The reaction was drastically influenced by the concentration of ammonium bromide. In order to obtain *cis*-$[CoBr(NH_3)(en)_2]Br_2$ in a good yield by this method, initial concentration of ammonium bromide should be more than 40 wt%. When the ammonium bromide concentration was less than 30 wt%, *cis*-$[CoBr(NH_3)(en)_2]Br_2$ could not be obtained. Concentrations of ammonium bromide for Runs 5, 11, 13 (42.3 wt%) and 3, 9 (28.2 wt%) illustrate this. Comparing the results of Runs 4 and 10, 5 and 11, 6 and 12, we show that increasing the amount of *cis*-$[Co(H_2O)(OH)(en)_2]Br_2$ reduces the yield of *cis*-$[CoBr(NH_3)(en)_2]Br_2$. The yields, however, were improved if the reaction time was increased as shown in Runs 13 and 14.

Pure, crystalline *cis*-$[CoBr(NH_3)(en)_2]Br_2$ was isolated from the reaction mixture obtained under the reaction conditions specified in Run 14 of Table I. The crystals were identified as *cis*-$[CoBr(NH_3)(en)_2]Br_2$ by absorption spectrum[15] and elemental analysis.[16] The yield of the isolated crystalline complex was 51.2%.

Acknowledgments

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References

[1] A. Werner and W.E. Boes, *Ann.*, **386**, 178 (1912).
[2] A. Werner, *Ann.*, **386**, 176 (1912).
[3] A. Werner, *Ann.*, **386**, 179 (1912).
[4] M.L. Tobe and D.F. Martin, *Inorg. Synth.*, **8**, 198 (1966).
[5] A. Werner, *Ber.*, **40**, 1887 (1911).
[6] G.B. Kauffman and E.V. Lindley Jr., *J. Chem. Educ.*, **51**, 424 (1974).
[7] I. Bernal, J. Cetrullo and W.G. Jackson, *Inorg. Chem.*, **32**, 4098 (1993).
[8] H. Nakagawa, S. Ohba, K. Asakura, T. Miura, A. Tanaka and S. Osanai, *Acta Crystallograph.*, **C53**, 216 (1997).
[9] K. Asakura, K. Kobayashi, Y. Mizusawa, T. Ozawa, S. Osanai and S. Yoshikawa, *Physica D*, **84**, 72 (1995).
[10] K. Asakura and S. Osanai, *Nippon Kessho Gakkaishi*, **38**, 229 (1996).
[11] K. Asakura, K. Kobayashi, Y. Mizusawa, T. Ozawa, T. Miura, A. Tanaka, Y. Kushibe and S. Osanai, *Recent Research Developments in Pure & Applied Chemistry*, **1**, 123 (1997).
[12] H. Kobayashi, K. Ohki, I. Tsujikawa, K. Osaki and N. Uryu, *Bull. Chem. Soc. Jpn.*, **49**, 1210 (1976).
[13] R.D. Cannon and J.E. Earley, *J. Am. Chem. Soc.*, **88**, 1872 (1965).
[14] Absorption spectra of *cis*- and *trans*-$[Co(H_2O)(OH)(en)_2]Br_2$ are identical, and the results are interpreted that both isomers readily rearrange to an equilibrium mixture: F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).
[15] λ_{max}: 542 nm, ε: 80.0 $mol^{-1}dm^3cm^{-1}$(λ_{max}: 540 nm, ε: 81 $mol^{-1}dm^3cm^{-1}$: (a) R.S. Nyloholm and M.L. Tobe, *J. Chem. Soc.*, **1956**, 1707. (b) J.F. Remar, and D.E. Pennington and A. Haim, *Inorg. Chem.*, **4**, 1832 (1965)).
[16] Anal. Calcd. for $[CoC_4H_{16}N_4NH_3Br]Br_2$(%): C, 11.02; H, 4.39; N, 16.07; Br, 54.99. Found: C, 11.26; H, 4.23; N, 15.93; Br, 54.28.