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Note

The deaquation and anation reactions of some anionoaquobis(ethylenediamine)cobalt (III) complexes*

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The thermal deaquation and anation reactions of several *cis*- and *trans*-$[Co(en)_2(H_2O)_2]X_3 \cdot nH_2O$, ($X = Cl^-$, Br^-, and NO_3^-) complexes have previously been investigated by Chang and Wendlandt[1]. It was found that the chloride complexes generally deaquated to give the *cis*-$[Co(en)_2Cl_2]Cl$ complexes while the bromide complexes either gave the *cis*-product or a mixture of *cis*- and *trans*- complexes. We wish to report here additional thermal deaquation studies of the *cis*-$[Co(en)_2XY]Y \cdot H_2O$ and *cis*-$[Co(en)_2(H_2O)X]Y_2 \cdot H_2O$ complexes, where X is Cl^- or Br^- and Y is Br^- or NO_3^-.

EXPERIMENTAL

Preparation of compounds

The compounds, *cis*-$[Co(en)_2(H_2O)Cl]Br_2 \cdot H_2O$ and *cis*-$[Co(en)_2ClBr]Br_2 \cdot H_2O$, were prepared as previously described by Vaughn and Lindholm[2]. The *cis*-$[Co(en)_2(H_2O)Br]Br_2 \cdot H_2O$ was prepared from *cis*-$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$ by heating the latter at 40°C with just enough water to give complete dissolution. After the solution turned to a violet color, the former complex was precipitated by the addition of solid sodium bromide. The dark violet colored crystals were filtered off, washed with small portion of 95% ethanol followed by diethyl ether, and then air-dried at room temperature for 24 h. The complex, *cis*-$[Co(en)_2(H_2O)Cl](NO_3)_2$, was prepared by the reaction of *cis*-$[Co(en)_2(H_2O)Cl]Cl_2$ with silver nitrate, as previously described[3].

Analysis of the complexes gave the following results: *cis*-$[Co(en)_2(H_2O)Cl]Br_2 \cdot H_2O$; Co, 14.36% theor., 14.8% found; H_2O, 8.78% theor., 8.6% found. *cis*-$[Co(en)_2ClBr]Br \cdot H_2O$: Co, 15.02% theor., 15.4% found; H_2O, 4.59% theor., 4.1% found. *cis*-$[Co(en)_2(H_2O)Br]Br_2 \cdot H_2O$: Co, 12.96% theor., 12.9% found; H_2O, 7.92% theor., 7.9% found. *cis*-$[Co(en)_2(H_2O)Cl](NO_3)_2$: Co, 16.53% theor., 16.2% found; H_2O, 5.05% theor., 5.0% found.

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Thermoanalytical techniques

The TG and DTA data were obtained using the apparatus and procedures previously described[1].

RESULTS AND DISCUSSION

The TG and DTA curves of the complexes are given in Fig. 1, while the procedural thermal stability ranges are given in Table I.

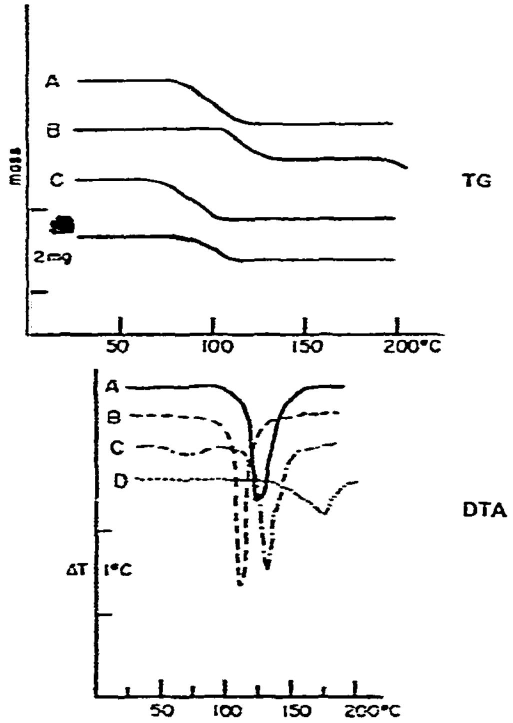

Fig. 1. TG and DTA curves of cobalt(III) complexes; (A) *cis*-[Co(en)$_2$(H$_2$O)Cl]Br$_2$·H$_2$O, (B) *cis*-[Co(en)$_2$(H$_2$O)Cl](NO$_3$)$_2$, (C) *cis*-[Co(en)$_2$(H$_2$O)Br]Br$_2$·H$_2$O, and (D) *cis*-[Co(en)$_2$ClBr]Br·H$_2$O.

TABLE I

PROCEDURAL THERMAL STABILITY TEMPERATURE RANGES OF COBALT(III) COMPLEXES

Complex	*Reaction interval, $T_i - T_f$ (°C)*	*Probable product(s)*
cis-[Co(en)$_2$(H$_2$O)Cl]Br$_2$·H$_2$O	75–125	*cis*- + *trans*-[Co(en)$_2$ClBr]Br
cis-[Co(en)$_2$(H$_2$O)Cl](NO$_3$)$_2$	105–130	*cis*- + *trans*-[Co(en)$_2$ClNO$_3$]NO$_3$
cis-[Co(en)$_2$(H$_2$O)Br]Br$_2$·H$_2$O	70–103	*cis*- + *trans*-[Co(en)$_2$Br$_2$]Br
cis-[Co(en)$_2$ClBr]Br·H$_2$O	80–112	*cis*-[Co(en)$_2$ClBr]Br

A single-step deaquation reaction was observed for all of the complexes. Hence, it was impossible to differentiate between the coordinated and the hydrate-bound water in those compounds containing both types of water molecules. The products, in all cases, were the dianionobis(ethylenediamine)cobalt(III) complexes, obtained according to the following reactions:

$$cis\text{-}[Co(en)_2(H_2O)X]Y_2\cdot H_2O(s) \rightarrow cis\text{-} + trans\text{-}[Co(en)_2XY]Y(s) + 2H_2O(g)$$
$$cis\text{-}[Co(en)_2(H_2O)X]Y_2(s) \rightarrow cis\text{-} + trans\text{-}[Co(en)_2XY]Y(s) + H_2O(g)$$
$$cis\text{-}[Co(en)_2XY]Y\cdot H_2O(s) \rightarrow cis\text{-}[Co(en)_2XY]Y(s) + H_2O(g)$$

For the *cis*-$[Co(en)_2(H_2O)Cl]Br_2\cdot H_2O$ complex, the formation of a mixture of *cis*- and *trans*-$[Co(en)_2ClBr]Br$ by thermal deaquation and anation has previously been reported as a synthetic method for the latter by Vaughn and Lindholm[2]. Accordingly, the pale green colored mixture of *cis*- and *trans*-$[Co(en)_2ClNO_3]NO_3$ obtained by the thermal deaquation of *cis*-$[Co(en)_2(H_2O)Cl](NO_3)_2$ provided a convenient synthesis for the preparation of the former compound. No attempt was made to isolate the two individual isomers from the mixture.

All of the complexes deaquated in the 70–130 °C temperature range; the least stable thermally appeared to be the *cis*-$[Co(en)_2(H_2O)Br]Br_2\cdot H_2O$ complex, while the most stable was the *cis*-$[Co(en)_2(H_2O)Cl](NO_3)_2$ complex. The dissociation temperatures were in the same range as the *cis*-$[Co(en)_2X_2]X\cdot H_2O$ complexes previously reported[1].

The DTA curves of the complexes, as given in Fig. 1, all contained a single endothermic peak with a ΔT_{min} in the temperature range from 115–185 °C. Because of the nature of the DTA sample holder, the procedural dissociation temperatures were somewhat higher in the DTA experiments than those obtained by TG measurements. Both *cis*-$[Co(en)_2(H_2O)Cl]Br_2\cdot H_2O$ and *cis*-$[Co(en)_2(H_2O)Cl](NO_3)_2$ had a single endothermic peak in their DTA curves, with ΔT_{min} values of 125 and 115 °C, respectively. The curve for *cis*-$[Co(en)_2ClBr]Br\cdot H_2O$ also contained a single endothermic peak with a ΔT_{min} for the endothermic peak at 179 °C which was similar to the ΔT_{min} values of 182 and 185 °C previously reported[1] for *cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$ and *cis*-$[Co(en)_2Br_2]Br\cdot H_2O$, respectively.

It was observed in several of the isothermal experiments that the change in configuration of the complexes, *cis* → *trans*, for example, was influenced by the experimental conditions in the furnace chamber. Using lower temperatures (longer reaction time required) and low concentrations of water vapor, the *cis*-product was preferentially obtained. The product, *cis*-$[Co(en)_2Br_2]Br$, was obtained from *cis*-$[Co(en)_2(H_2O)Br]Br_2\cdot H_2O$ by deaquation in a desiccator over potassium hydroxide at 50 °C *in vacuo*.

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