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THE HIGH-TEMPERATURE REFLECTANCE SPECTRA OF $[Co(NH_3)_5H_2O]X_3$ AND $[Cr(NH_3)_5H_2O]X_3$ COMPLEXES

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ABSTRACT

The HTRS and DRS of $[Co(NH_3)_5H_2O]X_3$ and $[Cr(NH_3)_5H_2O]X_3$ complexes were determined. The complexes undergo deaquation and anation reactions in the temperature range from 60 to 150 °C. A reflectance minima shift to longer wavelengths was observed on heating the aquopentammine complexes.

INTRODUCTION

The aquopentamminecobalt(III) and chromium(III) complexes are unstable in the solid-state due to the reaction:

$$[M(NH_3)_5H_2O]X_3(s) \rightarrow [M(NH_3)_5X]X_2(s) + H_2O(g) \quad (1)$$

The reaction takes place rather slowly at room temperature but proceeds quite rapidly in the temperature range from 75 to 100°C. Numerous studies have been carried out on these complexes. Jorgensen[1,3] and Werner[2] studied the cobalt(III) and chromium(III) complexes in order to develop a synthetic method for the preparation of $[Co(NH_3)_5X]X_2$ (X^- = Cl. Br, I and NO_3) and $[Cr(NH_3)_5X]X_2$ (X^- = Cl, Br, I and NO_3) type complexes. Mori and Tsuchida[4] and Wendlandt[5] reported the TGA curves for the $[Co(NH_3)_5H_2O]X_3$ complexes while Wendlandt and Bear[6] and Tsuchiya *et al.*[7] studied the $[Cr(NH_3)_5H_2O]X_3$ complexes by this technique. The complexes have also been studied by DTA by Lobanov *et al.*[8], Wendlandt and Bear[9] and others[6,7].

The kinetics and the heats of deaquation and anation have been determined by various investigators[4,6,7,9,10] but the results of these studies still present many unsolved problems. New data on the heats of deaquation and anation obtained by the "sealed-tube" DTA technique appear capable of resolving the qustions generated by the earlier data[11].

The reflectance curves of several of the cobalt(III) and chromium(III) complexes have previously been discussed[12,13], but a systematic investigation of these complexes at elevated temperatures has not been carried out. Accordingly, the complexes were studied by the HTRS (high temperature reflectance spectroscopy) and DRS (dynamic reflectance spectroscopy) techniques[14-16].

EXPERIMENTAL

Apparatus

The HTRS and DRS curves were obtained using the heated sample holder described by Wendlandt and Dosch[17]. The sample was contained in a 1 × 10 mm identation in the heated silver block; a static air atmosphere was present in the sample chamber. Reflectance measurements were made on a Beckman Model DK-2A spectroreflectometer using freshly prepared MgO as the reflectance standard.

Preparation of compounds

The complexes were prepared as previously described[6,9]. Water contents were determined by mass-loss on the thermobalance

DISCUSSION

Aquopentamminecobalt(III) complexes

The HTRS and DRS curves of $[Co(NH_3)_5H_2O]Cl_3$ are given in Fig. 1. For $[Co(NH_3)_5H_2O]Cl_3$, the reflectance curve at 23 °C contained a broad reflectance

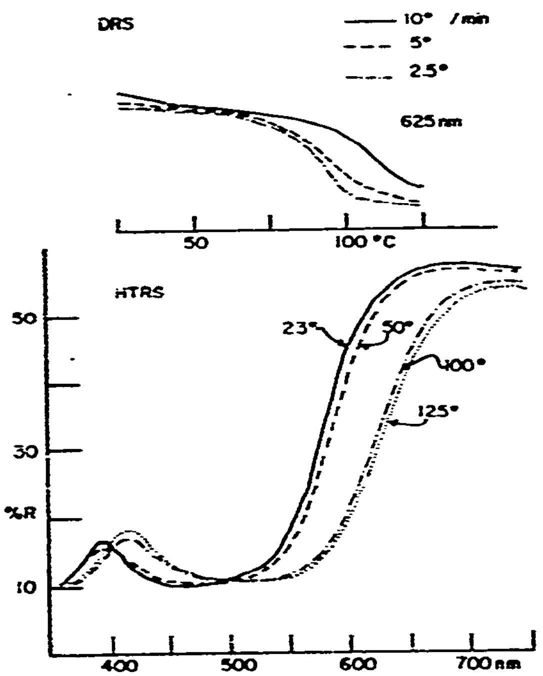


Fig. 1. HTRS and DRS curves for $[Co(NH_3)_5H_2O]Cl_3$. The DRS curves illustrate the effect of heating rate (values in °/min).

minimum at about 485 nm. On heating to 100 °C, the minimum shifted to about 525 nm. This shift is due to the deaquation and anation reaction; the 125 °C curve is that of $[Co(NH_3)_5Cl]Cl_2$ showing complete water evolution as given by Eqn. (1).

The temperature dependence of the deaquation reaction is shown by the DRS curves obtained at 625 nm. At a heating rate of 10°/min the reflectance gradually decreases in the 25–75°C temperature range and becomes more rapid above 75°C. At slower heating rates, say 5 or 2.5°/min, the curves are similar except that the deaquation reaction is completed at a lower temperature. At 2.5°/min, the deaquation reaction appears to take place only from 75° to 100°C.

The data for the other aquopentamminecobalt(III) complexes are given in Table I. The reflectance curves for $[Co(NH_3)_5H_2O]I_3$ did not contain curve minima as were present in the other complexes.

TABLE I

HTRS AND DRS DATA FOR $[Co(NH_3)_5H_2O]X_3$ COMPLEXES (DRS DATA AT 5°/MIN).

Compound	*Reflectance minima (nm)*		*Deaquation temperature interval*
	$[Co(NH_3)_5H_2O]X_3$	$[Co(NH_3)_5X]X_2$	
$[Co(NH_3]_5H_2O]Cl_3$	485	525	75–100°C
$[Co(NH_3)_5H_2O]Br_3$	500	570	75–125°C
$[Co(NH_3)_5H_2O]I_3$	[a]	[a]	60–100°C
$[Co(NH_3)_5H_2O](NO_3)_3$	480	500	80–150°C

[a] Not observed.

Aquopentamminechromium(III) complexes

The HTRS and DRS curves of $[Cr(NH_3)_5H_2O]Cl$ are given in Figs. 2 and 3.

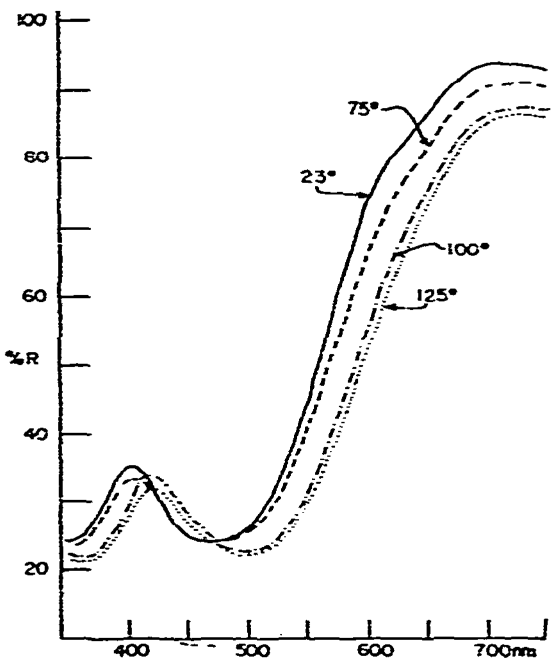
The HTRS curve of $[Cr(NH_3)_5N_2O]Cl_3$ contained a reflectance minimum of 475 nm at 23°C. On heating to 100°C, the minimum shifted to about 505 nm. The higher temperature curve is that of the deaquated complex, $[Cr(NH_3)_5Cl]Cl_2$. According to the DRS curve at 600 nm, the deaquation and anation reaction takes place between 75 and 110°C.

The HTRS and DRS data for the other $[Cr(NH_3)_5H_2O]X_3$ complexes are given in Table II.

TABLE II

HTRS AND DRS DATA FOR $[Cr(NH_3)_5H_2O]X_3$ COMPLEXES (DRS DATA AT 5°/MIN).

Compound	*Reflectance minima (nm)*		*Deaquation temperature interval*
	$[Co(NH_3)_5H_2O]X_3$	$[Co(NH_3)_5X]X_2$	
$[Cr(NH_3)_5H_2O]Cl_3$	475	505	75–110°C
$[Cr(NH_3)_5H_2O]Br_3$	470	525	85–120°C
$[Cr(NH_3)_5H_2O]I_3$	475	540	65–130°C
$[Cr(NH_3)_5H_2O](NO_3)_3$	475	490	80–130°C



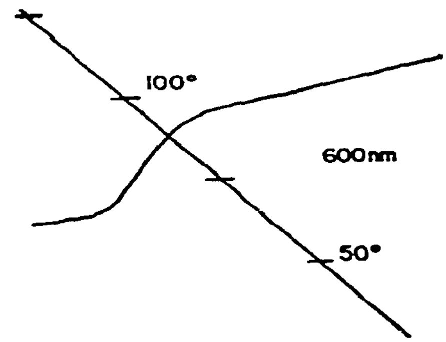


Fig. 2. HTRS curves of $[Cr(NH_3)_5H_2O]Cl_3$.

Fig. 3. DRS curve of $[Cr(NH_3)_5H_2O]C_3$; heating rate of 5°/min.

CONCLUSIONS

The $[Co(NH_3)_5H_2O]X_3$ and $[Cr(NH_3)_5H_2O]X_3$ complexes have deaquation and anation reactions in the temperature range from 60 to 150°C. The reflectance minima of the aquopentammine complexes shifts to higher wavelengths during the above reactions. The temperature measurement data were not sensitive enough so that any definitive conclusions concerning an order of thermal stability could be determined. The most stable of the cobalt(III) complexes appears to be $[Co(NH_3)_5H_2O](NO_3)_3$; for chromium(III) complexes, $[Cr(NH_3)_5H_2O]Br_3$ appeared to be the most thermally stable.

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