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THERMAL STUDIES ON TRANS-DICHLOROTETRAMMINECOBALT(III) COMPLEXES

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Thermal studies have been carried out on trans-$[Co(NH_3)_4Cl_2]X \cdot YH_2O$ complexes (where $X = IO_3$, BrO_3, NO_3, or NO_2 and $Y = 0$, 1, or 2) in an effort to find cases of trans to cis isomerization as occurs for the iodate. No evidence of isomerization was found for any of the other compounds. The complexes decompose in a series of steps and these reactions have been identified and kinetic parameters determined.

While there are several examples of trans to cis and cis to trans isomerization reactions which occur in solution, there are few reactions of this type which occur in the solid state [1]. Wendlandt et al., studied the decomposition of $[Co(NH_3)_4(H_2O)_2]Cl_3$ using DTA and reported two endothermic peaks during dehydration followed by an exothermic peak [2]. The third peak was attributed to a phase change or to geometrical isomerization, and it was presumed that trans-$[Co(NH_3)_4Cl_2]Cl$ formed and that it was converted to the cis isomer. Later, Watt and Butler observed that trans-$[Co(NH_3)_4Cl_2]Cl$ isomerizes upon heating in the solid state [3]. The most thoroughly studied isomerization of this type is that reported by Lobanov who reported that heating solid trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ causes dehydration and conversion to the cis isomer [4]. The DTA curve for trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ shows two endothermic peaks corresponding to dehydration and an exothermic peak which is reported to correspond to isomerization. This process was studied by LeMay and Bailer who found that attempts to dehydrate the complex by several techniques always led to isomerization [5]. These workers proposed an aquation-anation mechanism involving diffusion of the water of hydration through the crystal and thereby playing a role in the isomerization. A later study by LeMay and coworkers reported an activation energy of 14 ± 1 kcal/mole and an enthalpy of -15.2 ± 0.3 kcal/mole for the isomerization [6]. In view of the rather unique behaviour of trans-

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$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$, we have studied a series of complexes of the type trans-$[Co(NH_3)_4Cl_2]X \cdot YH_2O$ (where $X = NO_2, NO_3, BrO_3$, or IO_3 and $Y = 0, 1$, or 2) in an effort to identify other cases where isomerization may occur in the solid state. This report presents the results of that work.

Experimental

Preparation of compounds

Trans-dichlorotetramminecobalt(III) bisulfate was prepared by the method of Schlessinger [7]. The crystals were separated by filtration and washed with cold dilute HCl, 95% ethanol, and ether. The product was then allowed to dry in air.

Trans-dichlorotetramminecobalt(III) iodate dihydrate was prepared from trans-$[Co(NH_3)_4Cl_2]HSO_4$ by the method of Lobanov [4] with the modifications described by LeMay and Bailar [5]. The product was separated by filtration and washed with a 50% ethanol-water mixture, ethanol, and ether. The compound was then allowed to dry in air.

Trans-dichlorotetramminecobalt(III) bromate monohydrate was prepared by the method of Lobanov [8]. The green crystals were separated by filtration and washed in succession with 50% ethanol, 95% ethanol, and ether. The product was allowed to dry in air.

Trans-dichlorotetramminecobalt(III) nitrate monohydrate was prepared from the bisulfate by a previously described method [8]. The green crystals were treated as described above for the bromate. The nitrite compound was also prepared in a manner similar to the nitrate and purified in the same way.

Thermal studies

The decomposition of the complexes was studied using a Perkin–Elmer Thermogravimetric System Model TGS–2 controlled by a Perkin–Elmer Temperature Programmer Model UU–1. All runs were made in a dry nitrogen atmosphere. Heating rates of 5, 10, and 20 deg/min were used and sample sizes varied from 0.6–7.0 mg. Most samples were about 3 mg.

A Perkin–Elmer Differential Scanning Calorimeter Model DSC–2 was used to carry out the DSC studies. A scan rate of 10 deg/min was employed with samples maintained in a dry nitrogen atmosphere. In all cases, several runs were made and mean ΔH values were determined.

Kinetics methods

Kinetic parameters were determined from the TG data using the Coats and Redfern method [9] and the Reich and Stivala method [10]. The Coats and Redfern method was applied testing the values $n=0$, 1/3, 2/3,..., 2 for the rate law:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}(1-\alpha)^n e^{-E/RT} \tag{1}$$

where α is the fraction of reaction completed, T is the temperature (K), A is the frequency factor, E is the activation energy, β is the heating rate and R is the gas constant. Both the Coats and Redfern and the Reich and Stivala methods were applied using a microcomputer with programs written in BASIC.

Results and discussion

Of the compounds studied in this work, the iodate has been shown to isomerize during the dehydration process. In this work, the TG curves for trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ show a mass loss in the range of 40–140° with the actual temperature interval depending on the heating rate. For example, at 5 deg/min the dehydration took place between 40 and 120°, while at a heating rate of 20 deg/min the range was 70–140°. The observed mass loss was 6.8 ± 1.1% while the calculated value is 8.8%, indicating slightly less than two water molecules of crystallization. As has been previously reported, the DSC curves showed separated endothermic peaks corresponding to the dehydration and isomerization reactions. The ΔH for dehydration was found to be 80.8 ± 10.9 kJ/mole and the ΔH for isomerization is -55.6 ± 5.0 kJ/mole. In each case, the formula for the dihydrate is assumed to be correct although our preparation seemed to have somewhat less water of hydration. Analysis of the mass loss data for dehydration by the method of Coats and Redfern gave the best fit for an n value of 2 and yielded an activation energy of 57 ± 12 kJ/mole. Analysis of the data by the Reich and Stivala method gave a best n of 1.9 ± 0.3 with $E = 56 \pm 12$ kJ/mole. These values are in good agreement with previously reported data for these reactions. Subsequent decomposition of the anhydrous compound gave no identifiable intermediates.

The TG curve for the decomposition of trans-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$ is shown in Fig. 1. The DSC curve shows an endotherm corresponding to dehydration that indicates at ΔH of 45.2 ± 5.4 kJ/mole, which is typical for weakly bonded hydrates. The DSC curve showed a single endotherm in this temperature range, and there was no evidence of any peak corresponding to isomerization. From the observed mass losses, the decomposition appears to be

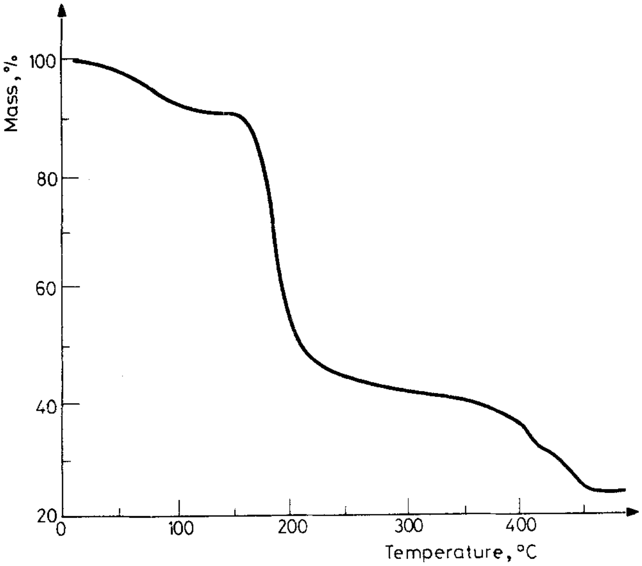

Fig. 1 TG curve for trans-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$

$$\text{Trans-}[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O(s) \rightarrow \text{Trans-}[Co(NH_3)_4Cl_2]BrO_3(s) + + H_2O(g) \tag{2}$$

$$\text{Trans-}[Co(NH_3)_4Cl_2]BrO_3(s) \rightarrow CoCl_2Br(s) + 3NH_3(g) + 3H_2O(g) + + 3/4\,O_2(g) + 1/2\,N_2(g) \tag{3}$$

The $CoCl_2Br$ decomposes in a two-step process which is approximated by the reactions

$$CoCl_2Br(s) \rightarrow CoCl_2Br_{3/4}(s) + 1/8Br_2(g) \tag{4}$$

$$CoCl_2Br_{3/4}(s) \rightarrow CoCl_2(s) + 3/8Br_2(g) \tag{5}$$

Mass loss and kinetic data for these reactions are shown in Table 1.

For trans-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$, the TG curve is shown in Figure 2. The DSC curve showed a single endotherm in the dehydration region with a ΔH of 54.0 ± 12.1 kJ/mole. As in the case of the bromate, there was no evidence of an enthalpy change due to isomerization. From the observed mass losses, the decomposition reactions appear to be

$$\text{Trans-}[Co(NH_3)_4Cl_2]NO_3H_2O(s) \rightarrow \text{Trans-}[Co(NH_3)_4Cl_2]NO_3(s) + H_2O(g) \tag{6}$$

Table 1 Mass loss data and kinetic parameters for decomposition reactions of trans-dichlorotetramminecobalt(III) complexes

Reaction	Mass loss, %		Coats and Redfern[a]		Reich and Stivala[b]	
	calcd.	found	n	E, kJ/mole	n	E, kJ/mole
			Trans-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$			
Eq. (2)	5.5	6.1±0.1	2	59± 8	2.34±0.60	74±15
Eq. (3)	43.7	43.4±0.1	0	92± 7	0.11±0.06	92± 7
Eq. (4)	6.1	5.8±0.1	2	254±45	2.39±0.47	290±63
Eq. (5)	18.3	15.9±5.2	2/3	97± 9	0.65±0.21	99±20
			Trans-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$			
Eq. (6)	6.5	6.8±0.4	2	62± 8	2.48±0.42	82±15
Eq. (7)	41.3	43.0±2.1	1/3	118±18	1.20±0.40	115±12
Eq. (8)	5.8	6.9±2.1	2	154±29	2.18±0.80	207±49
			Trans-$[Co(NH_3)_4Cl_2]NO_2$			
Eq. (9)	20.9	21.9±2.0	0	92±34	—	—
Eq. (10)	19.7	17.9±1.6	1/3	215±31	1.23±0.15	224±22
Eq. (11)	7.0	7.6±0.7	5/3	236±32	1.71±0.53	250±43

[a] Ref. [9].
[b] Ref. [10].

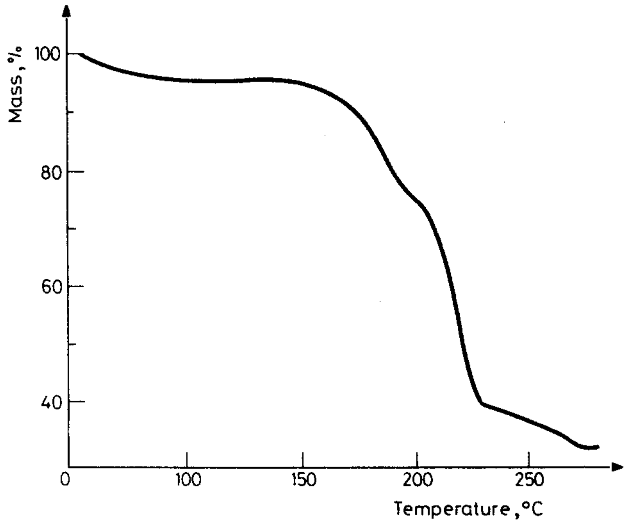

Fig. 2 TG curve for trans-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$

$$\text{Trans-}[Co(NH_3)_4Cl_2]NO_3(s) \rightarrow Co(NH_2)Cl_2(s) + 2NH_3(g) + 2H_2O(g) + N_2O(g) \qquad (7)$$

$$Co(NH_2)Cl_2(s) \rightarrow CoCl_2(s) + 1/2N_2H_4(g) \qquad (8)$$

The gaseous reaction products shown in Eq. (7) are identical to those reported by Wendlandt and Smith in the decomposition of $[Co(NH_3)_6](NO_3)_3$ [11]. Table 1 shows mass losses and kinetic parameters for these decomposition reactions of trans-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$.

The trans-$[Co(NH_3)_4Cl_2]NO_2$ as prepared in this work was found to be anhydrous. A typical TG curve for this compound is shown in Figure 3. The DSC curve showed no enthalpy change prior to decomposition. It appears, therefore, that no trans to cis isomerization occurs in the case of the nitrite compound. The observed mass losses correspond well to the reactions shown below.

$$\text{Trans-}[Co(NH_3)_4Cl_2]NO_2(s) \rightarrow Co(NH_3)Cl_2NO_2(s) + 3NH_3(g) \qquad (9)$$

$$Co(NH_3)Cl_2NO_2(s) \rightarrow Co(NH_3)Cl_2(s) + NO_2(g) \qquad (10)$$

$$Co(NH_3)Cl_2(s) \rightarrow CoCl_2(s) + NH_3(g) \qquad (11)$$

The mass loss data and kinetic parameters for these reactions are shown in Table 1.

It is interesting that of the compounds studied here, only the iodate compound undergoes an isomerization reaction. In a manner similar to the iodate complex, the nitrate and bromate compounds undergo dehydration reactions as the first step in

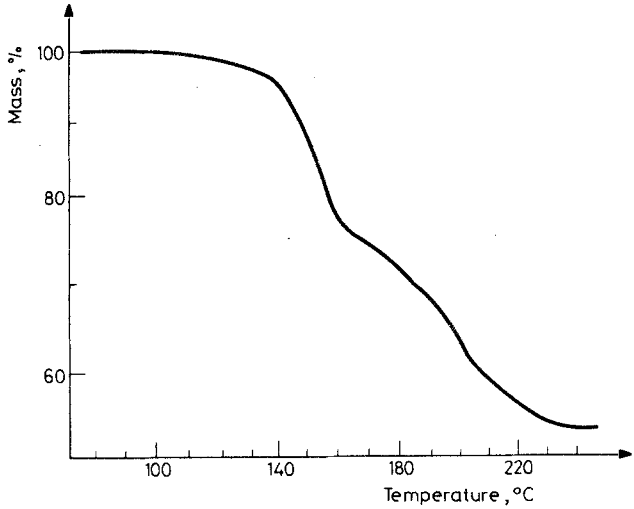

Fig. 3 TG curve for trans-$[Co(NH_3)_4Cl_2]NO_2$

the decomposition process. In general, all three complexes appear to follow an $n = 2$ rate law, but the analysis of the data obtained at different heating rates indicates a three-dimensional diffusion controlled mechanism [12].

Based on the DSC results, trans-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$ did not appear to undergo an isomerization reaction. It is likely that isomerization may not be possible due to the thermal instability of the complex. After dehydration, the decomposition process begins at a temperature of 140°. The isomerization reaction of trans-$[Co(NH_3)_4Cl_2]IO_3$ [4–6] does not occur until temperatures above 180°. Therefore, it appears that thermal decomposition of the nitrate compound occurs at temperatures below those at which isomerization would occur. Similarly, the decomposition of anhydrous trans-$[Co(NH_3)_2Cl_2]BrO_3$ begins at 130–150° depending on the heating rate. Lobanov reported that the bromate compound decomposes violently above 125° [8]. It is likely that in this case also the compound decomposes at temperatures below those at which isomerization would occur.

The nitrite complex was anhydrous, but it was more stable than either the bromate or the nitrate. However, there was no evidence of isomerization. Isomerization in the case of the iodate occurs during dehydration which may be related to lattice expansion as the water escapes [13]. With there being no water of hydration for the nitrite, this process may be prohibited or occur at higher temperatures. If an aquation-anation pathway is involved in the isomerization, the anhydrous compound would not be expected to isomerize. It is not known whether all these compounds have the same crystal structure or not. Differences in crystal structures may be a reason why only the iodate compound isomerizes.

This work has given new insight into the decomposition of trans-dichlorotetramminecobalt(III) complexes. Although the decomposition reactions of the iodate are uncertain, all of the other complexes studied gave $CoCl_2$ as the final solid product. Only the iodate has been found to undergo isomerization. We are currently investigating other features of the decomposition of these and similar complexes.

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Zusammenfassung — An trans-$[Co(NH_3)_4Cl_2]X \cdot YH_2O$ Komplexen (mit $X = IO_3$, BrO_3, NO_3, NO_2 und $Y = 0$, 1 oder 2) wurden thermische Untersuchungen durchgeführt, um Fälle einer Isomerisierung von trans zu cis zu finden, wie sie beim Jodat vonstattengeht. Bei den anderen Verbindungen konnte die Isomerisierung nicht nachgewiesen werden. Die Komplexe zerfallen in einer Reihe von Schritten, für die die Reaktionen identifiziert und die kinetischen Parameter bestimmt wurden.

Резюме — Термическое исследование комплексов транс-$[Co(NH_3)_4Cl_2]X \cdot YH_2O$, где $X = IO_3$, BrO_3, NO_3 или NO_2, а $Y = 0$, 1 и 2, было предпринято с целью обнаружения случаев транс-цис-изомеризации, наблюдаемой для иодата. Для других соединений не было обнаружено такой изомеризации. Комплексы разлагаются в несколько стадий и эти реакции были идентифицированы и определены их кинетические параметры.