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THERMAL DECOMPOSITION OF THE COMPLEXES $[Co(NH_3)_6][Nd(SO_4)_3] \cdot nH_2O$

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ABSTRACT

Thermal decomposition of the complexes, $[Co(NH_3)_6][Nd(SO_4)_3] \cdot nH_2O$ was studied by use of a DTA–TG instrument. On heating, all the complexes had been transformed to a mixture of anhydrous sulfates of Co(II) and Nd(III) by 400°C. At higher temperatures the sulfates were decomposed to their oxides independently. In air the transformation of Co(III) ammine to Co(II) sulfate occurred exothermically, while in argon the reaction was endothermic overall. Exceptionally, microcrystalline samples of the tetrahydrate decomposed endothermically. Various experiments indicated that the exotherm is due to an oxidative decomposition of the coordinated ammonia to nitrogen and water. This oxidation of ammonia and the causes of different decomposition reactions of the ammines are discussed.

INTRODUCTION

Thermal decomposition studies of transition metal ammine complexes to investigate the behavior of coordinated ammonia, the formation of intermediate complexes and the stoichiometry of decomposition on heating have been carried out [1–6]. In most cases it is reported that the principal reaction is an endothermic release of ammonia with formation of simple salts. In the case of Co(III) complexes particularly, reduction to Co(II) takes place simultaneously although its mechanism is not very clear [2,4,5].

We have studied the precipitation of crystalline compounds of rare earth elements and actinide elements with hexaamminecobalt(III) ion, obtaining insoluble crystalline compounds from aqueous solutions [7,8] and have found that trivalent lanthanide elements form complex compounds of formula $[Co(NH_3)_6][Ln(SO_4)_3] \cdot nH_2O$. We have also studied thermal decomposition of some of the actinide complexes by DTA or TG techniques [9], but little information on the mechanism of deamination was obtained, because of the difficulty of running experiments with actinide elements under various conditions.

In the present study, DTA–TG measurements were made for Nd(III) sulfato complexes, $[Co(NH_3)_4][Nd(SO_4)_3] \cdot nH_2O$ ($n = 4$ and 5). In an air

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flow a deamination reaction occurred with a large heat evolution, whilst in an argon flow it occurred endothermically. In addition, it was found that the crystallinity of the tetrahydrate influences the mode of the decomposition reaction.

EXPERIMENTAL

Preparation of the complexes

The complexes were prepared by adding hexaamminecobalt(III) chloride solution to 0.2 M ammonium sulfate or sulfuric acid solutions containing 2–5 mg Nd(III) ml^{-1}. On vigorous stirring, a brown precipitate formed immediately (complex A). The precipitate was filtered after 15–30 min agitation using a sintered-glass filter crucible and washed with water and alcohol. Further agitation of the unfiltered solution for a few hours gave a voluminous and pink precipitate (complex B). When the solution was not stirred at all, orange-red crystals gradually appeared (complex C). After a few days, it was removed from the solution and washed as described above. These three complexes were analysed for Co by colorimetry with nitroso-R salt, for Nd by compleximetric titration with EDTA, and for SO_4^{2-} by gravimetric analysis as $BaSO_4$. The results indicated that all complexes can be represented as $[Co(NH_3)_6][Nd(SO_4)_3] \cdot nH_2O$. Elemental analysis: A; calcd. for pentahydrate: Co, 8.62; Nd, 21.10; SO_4, 42.15; H_2O, 13.18. Found: Co, 8.84; Nd, 21.14; SO_4, 41.60; H_2O, 13.10. B and C; Calcd. for tetrahydrate: Co, 8.85; Nd, 21.67; SO_4, 43.40; H_2O, 10.83. Found for B (and C): Co, 9.21 (9.31); Nd, 21.59 (22.16); SO_4, 43.82 (43.50); H_2O, 9.40 (8.89).

Thermal analysis

A DTA–TG instrument (high temperature type Thermoflex, Rigaku Denki Co.) which can move from room temperature to 1500°C and records differential temperature and weight change simultaneously, was used. Air or argon flowed upward around the vertical sample holder in the internal core of 2 cm diameter. The temperature was measured by a Pt–Pt/13% Rh thermocouple at the sample side. Thermocouples to detect temperature difference were located at the bottom of each plate on which the sample and the reference holders were placed. Samples of about 25 or 50 mg were packed in a platinum crucible diameter 0.5 cm and height 0.5 cm. Alpha-alumina was used as a reference material throughout the experiments.

Analysis of gaseous products

Ammonia, water and nitrogen dioxide in the gaseous products were determined separately by heating the sample packed in a platinum dish in a quartz tube with a furnace controlled by a programmed temperature regulator. Heating rate, gas flow rate and other conditions were selected to simulate those used in the DTA–TG measurements as far as possible. Gaseous products were transferred by an atmospheric gas stream to the following traps; a $Mg(ClO_4)_2$ column for H_2O, 50 ml of a standardized 0.1 M HCl solution for NH_3 and a MnO_2 (on carrier activated granular for elemental analysis, E. Merck) column for NO_2. The ammonia evolved was determined by titration of the acid remaining and the others by direct weighing of the respective columns.

Infrared spectra and X-ray powder diffraction

Infrared spectra were measured by a Japan Spectroscopy Co. Model A-3 infrared spectrophotometer employing the KBr disk method. Powder diffraction patterns were recorded by a diffractometer Model SG-7, Rigaku Denki Co. Copper K_α radiation filtered with Ni foil was used and detected with a NaI(Tl) scintillation counter.

RESULTS

Characterization of the complexes

When solutions containing $[Co(NH_3)_6]^{3+}$, Nd(III) and SO_4^{2-} were vigorously stirred, complex A was precipitated as fine particles which settled rather quickly. If the complex was left in the solution it turned into voluminous, pink precipitate B. The analyses suggested that complex B is the same as complex C, which is slowly crystallized in the solution without agitation. IR spectra and X-ray powder patterns are reproduced in Figs. 1 and 2. The powder patterns show that complexes B and C have the same crystal structure but that the crystallinity of complex B is not as good as the other. The infrared spectral study of these complexes may give information on the nature of the sulfate coordination and also on how coordinated ammonia molecules interact with the counter ions [10]. The characteristic bands due to tetrahedral sulfate ion appear at around 1100(ν_3), 600(ν_4) and 980(ν_1) cm^{-1}, and the first two of these split depending on the nature of its coordination, thus allowing determination of the unidentate, bridging or chelating bidentate character of SO_4^{2-} [11]. The spectra of B and C show splitting of ν_3 into four and of ν_4 into three bands. Also two weak bands are observable at 960 and 480 cm^{-1} due to the infrared inactive vibrations. This suggests that the sulfate ions in complexes B and C have bridging bidentate character. On the other hand, the spectrum of complex A shows monodentate character, since the splitting of ν_3 is not as obvious as in the above case and ν_4 splits into two bands. The octahedral $[Co(NH_3)_6]^{3+}$ cation is surrounded by sulfate ions, free or coordinated to Nd^{3+}, and by water molecules. Therefore, the coordinated ammonia is possibly interacting with the oxygen of the surrounding molecules by hydrogen bonding as found for the complexes $[Co(NH_3)_6]MF_6$ ($M =$ trivalent transition metals) [12]. The

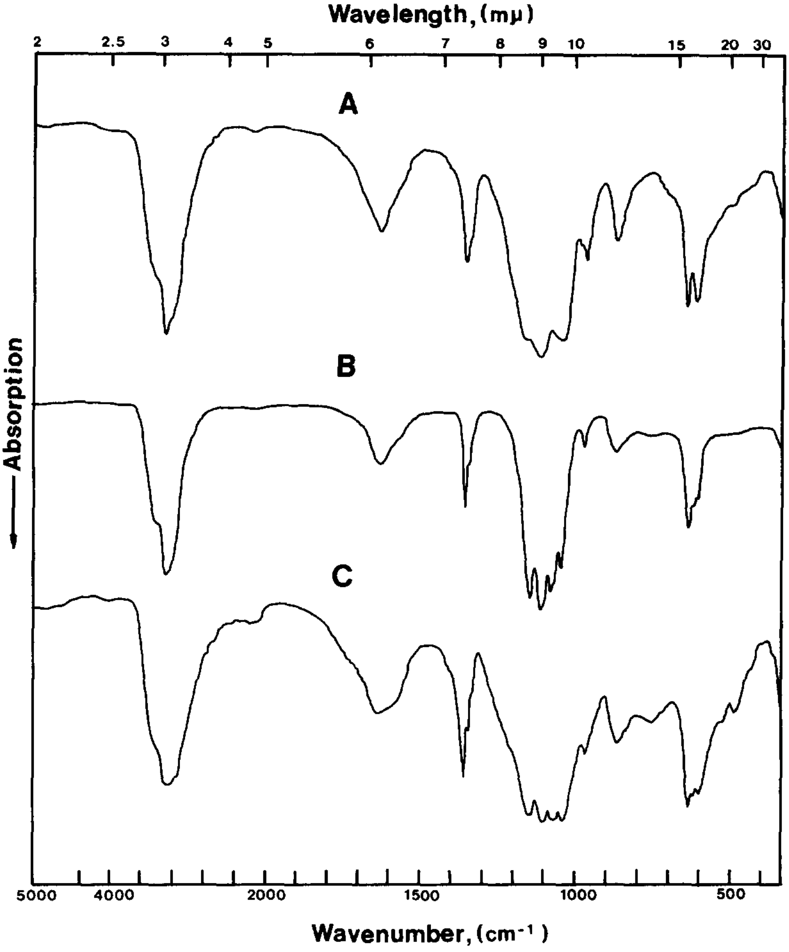

Fig. 1. Infrared spectra of the complexes A, B and C.

most sensitive vibrational mode for NH_3 is said to be the rocking mode which appears at 800–900 cm^{-1}. All spectra show an absorption at 860 cm^{-1}, shifted to higher frequencies than the values observed, for example $[Co(NH_3)_6]Cl_3$ (830 cm^{-1}).

DTA–TG measurements

Preliminary experiments showed that the decomposition of the complexes proceeds in three stages, i.e., firstly, dehydration at around 120°C, secondly, the decomposition of Co(III) ammine with formation of Co(II) sulfate and Nd(III) sulfate at about 300–400°C and finally the decomposition of the sulfates to their oxide or oxysulfate at 900–1000°C. The decomposition of the sulfates which occurred at the same temperatures as those observed for $CoSO_4 \cdot 7H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$ indicates that the product at the

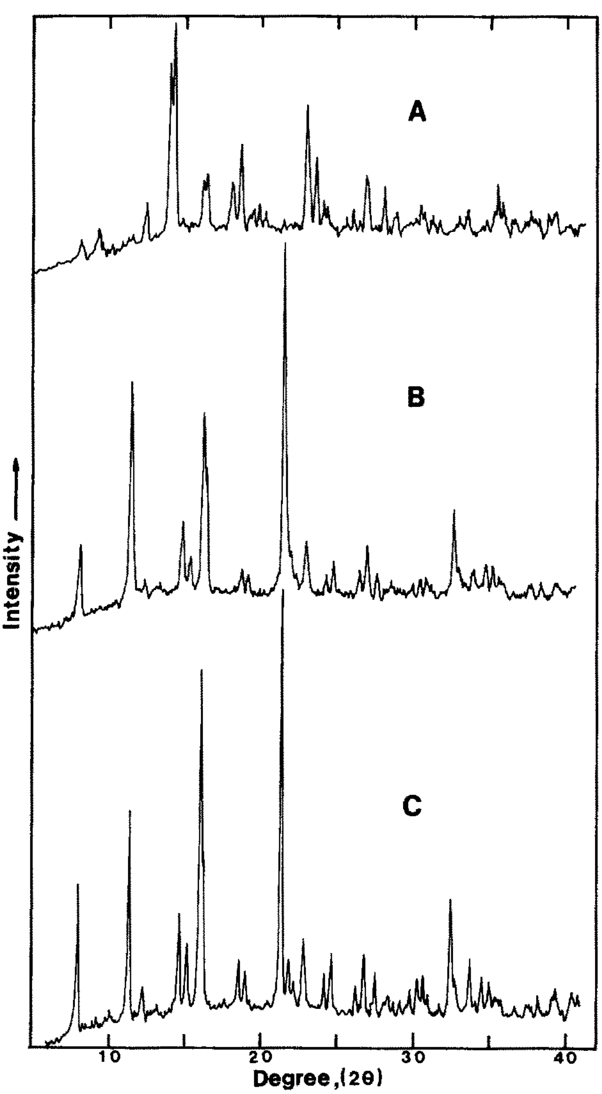

Fig. 2. X-ray powder diffraction patterns of the complexes A, B and C.

second stage is a mixture of two sulfates only. Thus detailed experiments were concentrated on the second stage decomposition.

In Fig. 3, DTA–TG curves for the complexes A, B and C in an argon gas flow of 100 ml $\min^{-1}$ are reproduced. In the inert atmosphere most transitions are endothermic. A small exotherm observed at around 400°C in each curve is probably due to the crystallization of $Nd_2(SO_4)_3$, which was found in the course of the thermal decomposition of $Nd_2(SO_4)_3 \cdot 8H_2O$ [13].

In Fig. 4, DTA–TG curves in an air flow of 100 ml $\min^{-1}$ are reproduced. For A and C, a remarkable difference from the curves obtained in an inert atmosphere is a large, characteristic exothermic peak at 200–400°C.

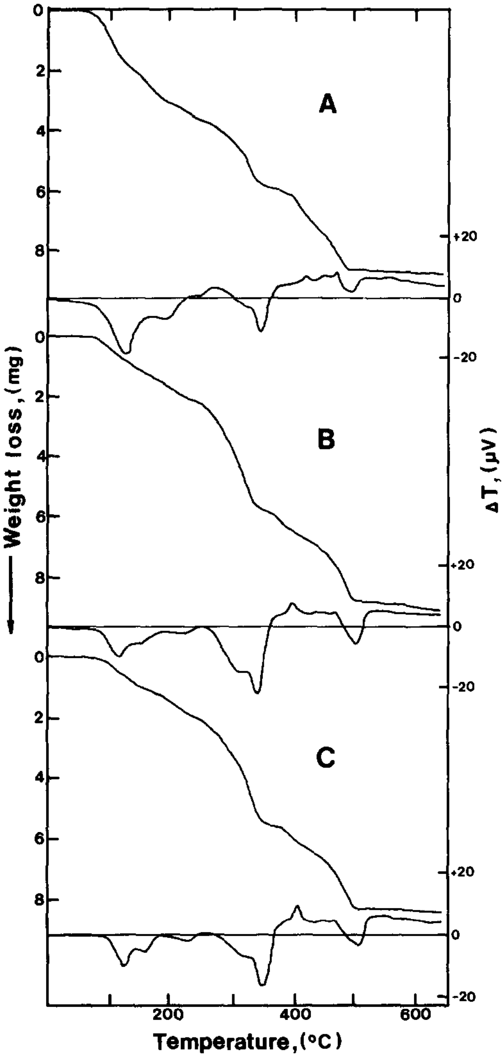

Fig. 3. DTA–TG curves of the complexes A, B and C in an argon gas flow of 100 ml min^{-1}; heating rate, 10°C min^{-1}.

Though the two exotherms look rather different, the initiation temperature and the maxima of the sharp peaks are very close, and it is possible that the decomposition reactions for the complexes may be similar. Moreover, it is interesting that the complexes B and C, which have the same composition and crystal structure, gave opposite thermal changes between 200 and 400°C.

In order to obtain further information on the exothermic decomposition of the complexes, DTA–TG measurements were carried out under various heating rates, air flow rates and oxygen content in the argon flow system.

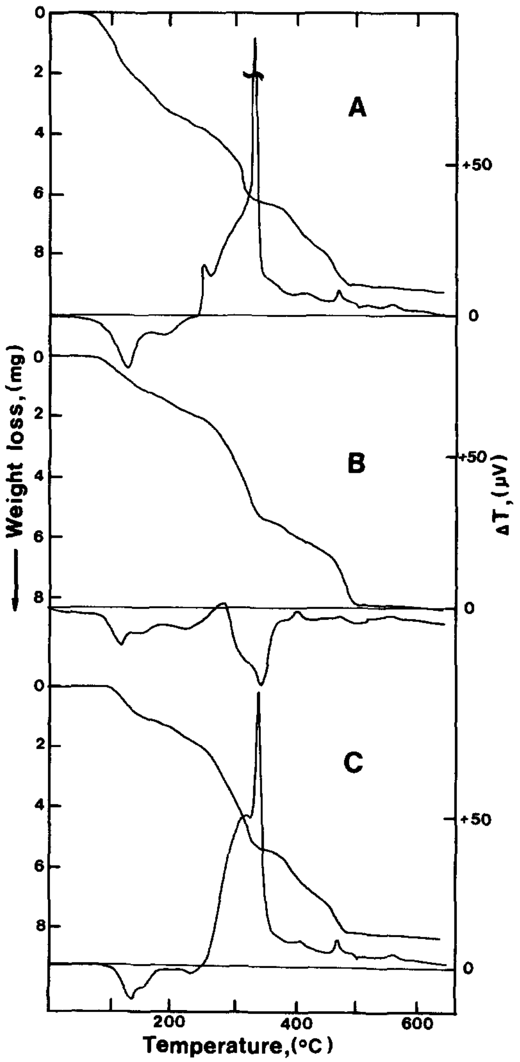

Fig. 4. DTA–TG curves of the complexes A, B and C in an air flow of 100 ml min^{-1}; heating rate, 10°C min^{-1}.

The results are shown in Figs. 5, 6 and 7. Under a constant air flow rate of 100 ml min^{-1} the DTA–TG apparatus was run at various heating rates (Fig. 5). Curves were quite similar at 5 and 10°C min^{-1}, whereas at 20°C min^{-1} the DTA curve is much more complicated. At this rate of heating heat evolution starts at 226°C and thus the temperature difference reaches its maximum at 319°C. Sudden endothermic, exothermic, endothermic and exothermic changes then occur successively in the very narrow temperature range from 319 to 347°C. As shown in Fig. 6, the DTA curve is more complicated in a static air atmosphere: the second sharp exothermic peak

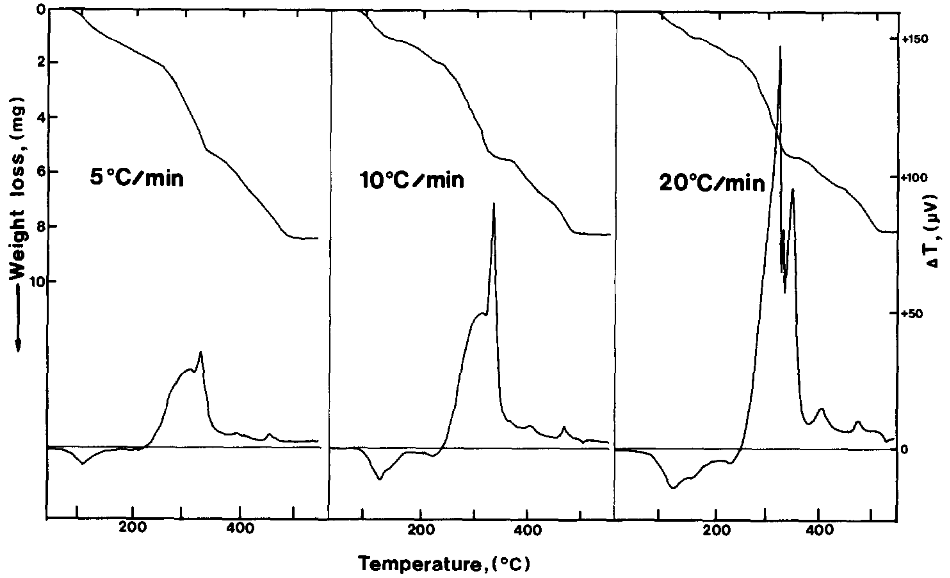

Fig. 5. Effect of the heating rate on the DTA–TG curve of complex C; air flow rate, 100 ml min^{-1}.

observed under this condition is missing in the DTA curve obtained in a dynamic air atmosphere. The fast recovery of the exothermic temperature difference for every case indicates that an endothermic change occurs at about 320°C. Since the peak temperatures for the first endotherm (117 ± 2°C) and the second exotherm (324 ± 4°C) do not differ at various flow rates, DTA–TG curves were obtained under varying oxygen content of an argon flow at the total rate of 200 ml min^{-1}. The oxygen flow rate was controlled with a precision microvalve and flowmeter. As seen in the Figure, the decomposition over the temperature range of 240–410°C, which proceeds endothermically without oxygen, evolves more heat as the oxygen content increases. It also appears that there is a definite oxygen content threshold beyond which the complex decomposes in the same way.

Evolved gas analysis

Gaseous products evolved on heating ca. 300 mg of the samples up to 550°C and holding at this temperature for an hour were determined. The results for NH_3 are given in Table 1. In an argon atmosphere similar fractions of the coordinated ammonia were released as NH_3 for all the samples A, B and C. In an air atmosphere, however, the complexes A and C which gave exothermic peaks at around 300°C released only a minor fraction of their NH_3. Since the weight change in an MnO_2 column was very small for each complex, the remaining ammonia must be converted to N_2 and water. Actually almost the equivalent amount of water (in addition to

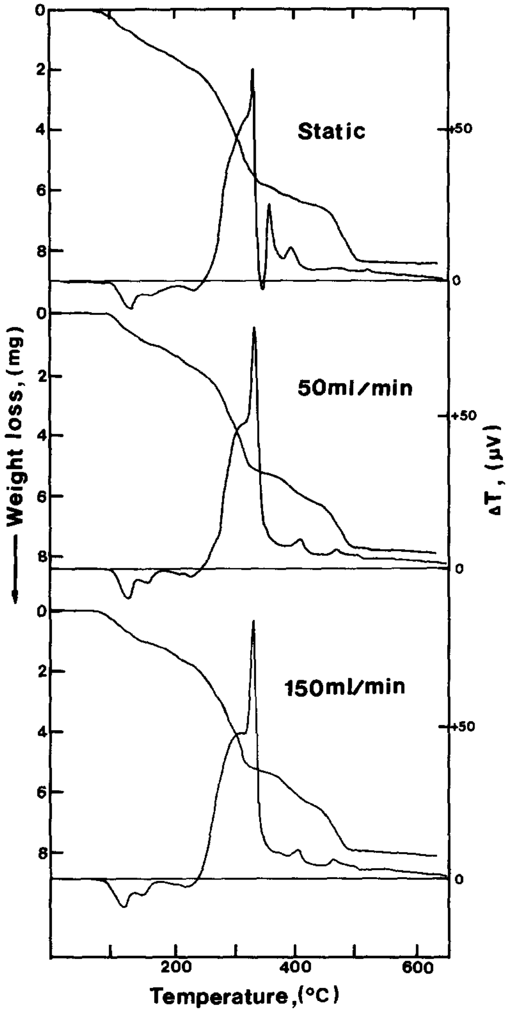

Fig. 6. Effect of the air flow rate on the DTA-TG curve of complex C; heating rate, 10°C min^{-1}.

TABLE 1

Amount of NH_3 evolved on heating

Complex	NH_3 evolved	
	in air (%)	in argon (%)
A: $[Co(NH_3)_6][Nd(SO_4)_3]\cdot 5H_2O$	7.7	79.3
B: $[Co(NH_3)_6][Nd(SO_4)_3]\cdot 4H_2O$	69.4	75.2
C: $[Co(NH_3)_6][Nd(SO_4)_3]\cdot 4H_2O$	12.2	75.3
$[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$	68.0	81.8

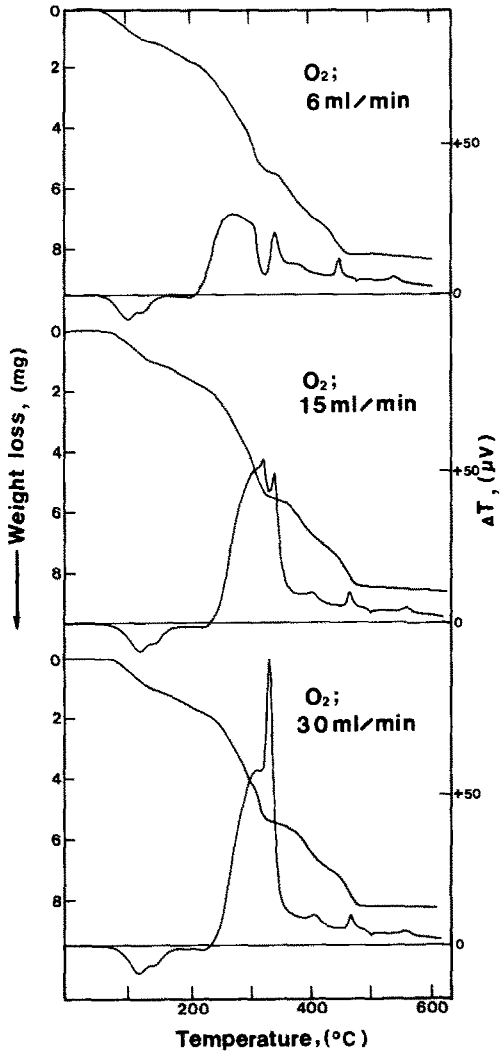

Fig. 7. Effect of addition of oxygen to the argon flow on the DTA-TG curve of complex C; total gas flow rate, 200 ml min^{-1}, heating rate, 10°C min^{-1}.

the water of crystallization) was trapped in the $Mg(ClO_4)_2$ column set up next to the MnO_2 column. Only complex B which decomposed endothermically in an air atmosphere, liberated 70–80% of its NH_3 without oxidation.

DISCUSSION

Thermal decomposition of various salts and double complexes containing the hexaamminecobalt(III) cation have been studied by many authors. Since most of the studies were carried out in an inert atmosphere exothermic changes due to the decomposition of ammines has rarely been observed

TABLE 2

Estimated heat of decomposition

Complex	q (kJ)	
	in air	in argon
A: $[Co(NH_3)_6][Nd(SO_4)_3]\cdot 5H_2O$	−829(−138)	175(29.2)
B: $[Co(NH_3)_6][Nd(SO_4)_3]\cdot 4H_2O$	351 (58.5)	380(63.3)
C: $[Co(NH_3)_6][Nd(SO_4)_3]\cdot 4H_2O$	−954(−159)	272(45.2)
$[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$	514 (42.8)	679(56.6)

q = heat adsorbed or evolved per formula amount of the complexes. Values in parentheses are those for 1 mol of NH_3.

except for the complexes containing nitrate. The coincidence of the results of evolved gas analysis with the DTA curve of each complex leads to the conclusion that the overall reaction which gives a large exothermic peak between 200 and 400°C is mainly the oxidation of NH_3 to N_2 and water, according to the reaction

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$$

This reaction is thermodynamically favored even at room temperature [14]. The heat change shown by DTA peaks for the deamination reaction was estimated by the peak area method using $LiNO_3$, $NaNO_3$ and KNO_3 as standard materials [15] (Table 2). The enthalpy change of the deamination for various ammine complexes is reported to be about 42 kJ mol^{-1} of NH_3 [16]. Comparing the values obtained for the complex B and $[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$ either in air or in argon, it is found that the amount of heat absorbed per mole of NH_3 is almost identical. Including the values obtained for the other complexes in an argon atmosphere, an average of 53 ± 9 kJ mol^{-1} of NH_3 can be calculated. This agreement suggests that the endothermic processes occurring in both atmospheres are the same. Wendlandt reported the decomposition stoichiometry of hexaamminecobalt(III) sulfate in a He atmosphere as [1]

$$6[Co(NH_3)_6]_2(SO_4)_3\cdot 2.5H_2O(s) \rightarrow 12CoSO_4(s) + N_2(g) + 6(NH_4)_2SO_4(s) + 56NH_3(g) + 15H_2O(g)$$

According to this, 78% of the coordinated ammonia is released as gas. The percentages obtained for the complexes in an argon atmosphere agree well, whereas those for B and $[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$ in an air atmosphere are lower by 10%. This discrepancy is not small enough to attribute to experimental error. The same reaction which causes exothermic change in the decomposition of A and C occurs, but to a smaller extent. The standard enthalpy change for the oxidation of NH_3 is 314 kJ mol^{-1} at 25°C [17]. Therefore, if all the ammonia is oxidized to N_2 after being released, 1630 kJ of heat will be evolved per mol of the complex. As given in the Table the observed heat evolution is 954 kJ mol^{-1}, equal to 60% of the former figure.

Since the fraction of NH_3 evolved is only 12%, this simple calculation does not give good agreement. However considering that the estimation for the large exotherm tends to give rather low values this disagreement does not disprove the oxidation of NH_3.

Since the complexes A and C decompose exothermically in air atmosphere only, the oxidation possibly occurs in the gas phase after release from the solid phase. However this does not accord with the following experimental results: (i) $[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$ undergoes endothermic transformation to $CoSO_4$ over a slightly lower temperature range from 200 to 290°C with liberation of 70% NH_3; (ii) in the same system an equimolar mixture of $[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$ showed only endothermic peaks at 200 and 300°C which were due mainly to dehydration and deamination respectively; (iii) the air flow rate did not affect the shape and the position of the exothermic peaks at all; even in static air atmosphere, the exothermic reaction proceeded at the same temperature.

Twenty-five mg of the Nd complex contains 2.3×10^{-4} mol NH_3, which will occupy 9.3 ml if it is released as a gas at 300°C. The empty space in the crucible above the sample is only 0.05 ml. In all the measurements, the second stage decomposition occurred over a temperature range of 220 to 350°C and lasted for about 10 min at the heating rate of 10°C min^{-1}. The total weight loss in this range amounts to about 3 mg, which corresponds to 78% of the total NH_3. On analysis of the TG curves, we found that: (i) at constant air flow rate, the rate of the weight loss increases with increasing heating rates, but the DTA peak shape and position are not affected; (ii) at a constant heating rate, the air flow rate produced no difference in the rate of weight loss; the exothermic change occurred at the same temperature; (iii) there are no significant differences in the rate of weight loss obtained for B and C, either in air or argon atmospheres; (iv) as the O_2 content in the argon flow increases, the rate of weight loss increases slightly. If we assume the weight loss is caused only by the release of NH_3, we can estimate the average rate of NH_3 evolution from the solid phase. For example, complex C would evolve 1.0 ml of NH_3 per min at a heating rate of 10°C min^{-1} and an air flow rate of 100 ml min^{-1}. Thus it is probable that the evolved ammonia will be mixed with the air and oxidized. However in this situation the air flow rate may affect the shape and the area of the exothermic peaks considerably. The temperature difference is detected between the Pt plates on which the crucibles were placed. Therefore, it seems improbable that heat produced by the reaction in the gas phase surrounding the crucibles is reflected well enough to give the exotherms. Since the observed DTA curves showed good reproducibility, the gas phase oxidation is not probable.

It is well known that platinum catalyses the reaction between NH_3 and O_2 at high temperatures [14].

$$4NH_3(g) + 5O_2(g) = 4NO(g) + 6H_2O(g)$$

The crucibles, thermocouples and other parts of the apparatus used in the present study are made of either Pt or Pt/Rh alloy. Since the oxidation of NH_3 takes place on their surfaces, it will produce a temperature difference which is detectable as an exotherm. However this does not explain the endothermic decomposition of complex B. Moreover NO_2 was not detected in the trap when 300 mg of complex C was decomposed.

In order to find any indications of different decomposition mechanisms, infrared spectra of the samples at intermediate temperatures were measured. The complexes were heated to the temperature at which the exothermic or endothermic changes had just begun, then to that at which the DTA peaks reached their maximum and finally is that at which the reactions were completed. The samples were taken out immediately the temperature reached these points. Comparison of the spectra showed no differences and hence revealed no different intermediates. It was found, however, that NH_4^+ was formed in the course of the decomposition since the spectra from samples at the first two temperature points had a band at 1420 cm^{-1}.

Joyner has discussed the effect of crystal size on the decomposition of hexaamminecobalt(III) azide, and has concluded that the topographical effect made one of the two possible reactions predominant [18]. In this case azide ions are considered as a reducing agent for Co(III). The difference between B and C exists only in the crystalline state as stated in the former section; complex B is a very fine powder and complex C is composed of rather large crystals. Therefore, the topographical effect may be important in this case, but at this time data are too incomplete to describe detailed mechanisms for the two types of decomposition.

REFERENCES

1 W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 545.
2 W.W. Wendlandt and J.P. Smith, J. Inorg. Nucl. Chem., 25 (1963) 1267.
3 E.L. Simmons and W.W. Wendlandt, J. Inorg. Nucl. Chem., 28 (1966) 2187.
4 N. Tanaka and M. Nanjo, Bull. Chem. Soc. Jpn., 37 (1964) 1330.
5 N. Tanaka and K. Nagase, Bull. Chem. Soc. Jpn., 40 (1967) 546.
6 G.W. Watt, Inorg. Chem., 3 (1964) 325.
7 A. Saito and K. Ueno, J. Inorg. Nucl. Chem., 40 (1978) 803.
8 A. Saito and K. Ueno, J. Inorg. Nucl. Chem., 41 (1979) 503.
9 A. Saito and K. Ueno, J. Inorg. Nucl. Chem., 42 (1980) 1301.
10 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley, New York, 1978, p. 197.
11 K. Nakamoto, J. Fujita, S. Tanaka and M. Kabayashi, J. Am. Chem. Soc., 79 (1957) 4904.
12 K. Wieghardt and H. Siebert, J. Mol. Struct., 7 (1971) 305.
13 A. Saito, unpublished data.
14 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th edn., Wiley, New York, 1980, p. 416.

15 C. Duval, Thermal Methods in Analytical Chemistry, in G. Svehla, (Ed.), Comprehensive Analytical Chemistry, Vol VII, Elsevier, Amsterdam, 1976, p. 131.
16 S.J. Ashcroft and C.T. Mortimer, Thermochemistry of Transition Metal Complexes, Academic Press, New York, 1970, p. 233.
17 D.D. Wagman, W.H. Evans, V.B. Parker, S.M. Bailey, K.L. Churney and R.L. Nuttal, The NBS Tables of Chemical Thermodynamic Properties—Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units, American Chemical Society, Washington, DC, 1982.
18 T.B. Joyner, J. Phys. Chem., 74 (1970) 1552; 74 (1970) 1558; 74 (1970) 1563.