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Thermal Decomposition Reactions of Analogous Pentaamminenitrosylcobalt(III) Complexes

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The thermal behavior of five complexes, $[Co(NH_3)_6]Cl_3$ (**1**), $[Co(NH_3)_5NO_2]Cl_2$ (**2**), $[Co(NH_3)_5NO]Cl_2$ (**3**), $[(NH_3)_5Co\text{-}N(O)\text{-}NO\text{-}Co(NH_3)_5]Cl_4 \cdot 2H_2O$ (**4**), and $[(NH_3)_5Co\text{-}NO\text{-}ON\text{-}Co(NH_3)_5]Cl_4 \cdot 4H_2O$ (**5**), has been investigated. The pyrolysis-gaschromatographic technique has been successfully applied to the N_2- and N_2O-analyses of the gases evolved on the pyrolysis of the complexes. The thermal decomposition of these complexes is characterized predominantly by the reduction process of Co(III) to Co(II). In the simple nitrosyl **3**, the NO^- group reduces the Co(III) ion and dissociates as NO. As for the remaining complexes, a thermally induced transient-state tends to dissociate H^+ from the coordinated ammonia as follows: $Co^{III}\text{-}NH_3 \rightarrow [Co^{III}\text{-}NH_2^{\delta-} \cdots H^{\delta+}] \rightarrow Co^{II} + NH_2 + H^+$. The NH_2 species is subsequently decomposed as $NH_2 \rightarrow 2/3NH_3 + 1/6N_2$. Moreover, H^+ is captured by an anionic species and/or the NH_3 present in the system, that is, by Cl^- and NH_3 forming NH_4Cl in the case of **1**, by NO_2^- and NH_3 forming NH_4NO_2, which then decomposes to N_2 and H_2O, in **2**, and by $N_2O_2^{2-}$ forming $H_2N_2O_2$, which then decomposes to N_2O and H_2O, in **4**. The **5** complex undergoes an exothermic decomposition, affording a larger amount of N_2 and N_2O than those to be expected from the above stoichiometry, suggesting an oxidative behavior of the bridged, dimeric $(\text{-}NO\text{-}ON\text{-})^{2-}$ group towards ammonia.

Three isomeric compounds with the unitary composition of $[Co(NH_3)_5NO]X_2$, where $X = Cl$ or NO_3, have so far been isolated by the reaction of gaseous NO with an ammoniacal solution of cobalt(II) salt.[1,2] X-Ray diffraction studies have confirmed that the black isomer (Black salt), obtained when the reaction is carried out at −10 °C, is a monomeric nitrosyl complex in which a NO^- group is bound to the cobalt atom in a bent manner,[3] while the red isomer (Red-I salt), obtainable by a similar reaction carried out at room temperature, is a binuclear complex in which two of the $Co(NH_3)_5$ groups are bridged through a *cis*-hyponitrite group, $(\text{-}N(O)\text{-}NO\text{-})^{2-}$.[4] Recently Miki and Ishimori[2] have isolated another red isomer (Red-II salt) by reacting NO at *ca.* 0 °C with an ammoniacal cobalt(II) solution which had previously been exposed to air for 20 h at *ca.* 20 °C. On the basis of IR and ^{15}N-NMR spectral investigations, they have identified this isomer as a binuclear complex including a $(\text{-}NO\text{-}ON\text{-})^{2-}$ group bridging two cobalt atoms of $Co(NH_3)_5$ groups.

As these isomers are thought to include intermediary forms of the NO group in a variety of compounds, it seems that it would be interesting to clarify the chemical properties of these isomers. In this work, their pyrolytic behavior in the solid state has been investigated.

Experimental

Materials. $[Co(NH_3)_6]Cl_3$,[5] $[Co(NH_3)_5NO_2]Cl_2$,[6] $[Co(NH_3)_5NO]Cl_2$ (Black salt),[1] $[(NH_3)_5Co\text{-}N(O)\text{-}NO\text{-}Co(NH_3)_5]Cl_4 \cdot 2H_2O$ (Red-I salt),[2] and $[(NH_3)_5Co\text{-}NO\text{-}ON\text{-}Co(NH_3)_5]Cl_4 \cdot 4H_2O$ (Red-II salt)[2] were prepared according to the published procedure; they were identified by means of cobalt analyses and a study of their infrared spectra.

Measurements. Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves were recorded on a Rigaku Denki thermal analyzer, Model 8002. The measurements were carried out in a nitrogen atomosphere and at a heating rate of 5 °C/min. A 20-mg aliquot of the sample was used. The analyses of the gases evolved were carried out by means of TCD-gaschromatography using a YANAKO G 80 instrument equipped with a YANAKO G 1018 pyrolysis pippeter.[7] A 2.0-mg aliquot of the sample was injected into the pyrolysis pippeter, whose furnace had been kept at the desired temperature; the sample was pyrolyzed rapidly in a helium gas, and the gaseous products were then swept by the helium-gas carrier into the separation column. A stainless steel column (size, 1.5 m×3 mm i.d.; packing, Molecular Sieve 5A, 60/80 mesh or Porapak S, 50/80 mesh) was used. The column and TCD temperature were maintained at 50 °C and 60 °C respectively. The flow rate of carrier gas was 25 cm^3/min. The calibration curves for the N_2 and N_2O determinations were made by means of the direct injection of pure gas (0 to 0.25 cm^3) into the separation column using a microsyringe; the peak area was measured by means of an integrator. The amount of ammonia evolved was determined by trapping it through bubbling into a standard 0.05 M-sulfuric acid solution and by then titrating the excess acid with a standard 0.1 M-sodium hydroxide solution. The magnetic susceptibility measurements were carried out by the Faraday method. The instrument was calibrated using $[Ni(en)_3]S_2O_3$ as the standard.[8] The IR spectra were recorded on a KBr disk using a Hitachi 345 infrared spectophotometer.

Results

The TG and DSC curves of three isomers are reproduced in Fig. 1, while the analytical results of the gaseous products on pyrolysis are shown in Table 1 and Fig. 2.

As Fig. 1-a shows, Black salt exhibits three endothermic DSC peaks, with maximum temperatures at 135, 230, and 295 °C. Step-by-step weight-losses of 32.2, 6.2, and 7.1% are observed in the TG curve; these seem to correspond to the above DSC peaks. These losses are comparable to those of 31.1, 6.9, and 6.9% calculated by assuming the elimination of 3 mol of ammonia and 1 mol of nitrogen monoxide, of 1 mol of ammonia, and of one further mole of ammonia, respectively. Black salt is well characterized by the IR absorption due to the coordinated NO^- group at 1620 cm^{-1},[9] while the pyrolysis of Black salt at 180 °C resulted in leaving a compound which showed no characteristic absorption in the same range. The results of gas analyses are considered to indicate that,

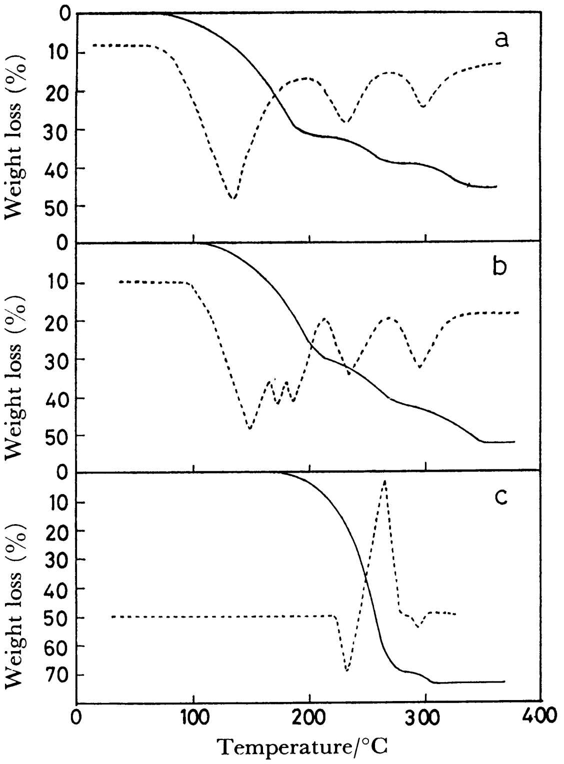

Fig. 1. TG and DSC curves obtained in nitrogen atmosphere.
a: $[Co(NH_3)_5NO]Cl_2$ (Black salt), b: $[Co_2(NH_3)_{10}N_2O_2]Cl_4 \cdot 2H_2O$ (Red-I salt), c: $[Co_2(NH_3)_{10}N_2O_2]Cl_4 \cdot 4H_2O$ (Red-II salt), TG: ——, DSC: ------.

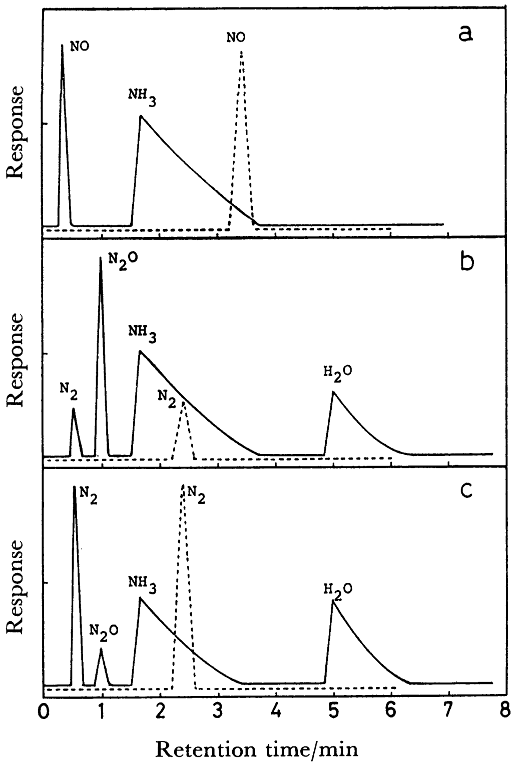

Fig. 2. Pyrolysis gaschromatograms.
a: $[Co(NH_3)_5NO]Cl_2$ (Black salt), pyrolyzed at 200 °C, b: $[Co_2(NH_3)_{10}N_2O_2]Cl_4 \cdot 2H_2O$ (Red-I salt), pyrolyzed at 290 °C, c: $[Co_2(NH_3)_{10}N_2O_2]Cl_4 \cdot 4H_2O$ (Red-II salt), pyrolyzed at 310 °C. Adsorbent: Porapak S: ——, molecular Sieve 5A: ------.

upon pyrolysis at 290 °C, 1 mol of Black salt produces almost quantitatively 1 mol of nitrogen monoxide and 5 mol of ammonia.

The DSC curve of Red-I salt is rather more complicated than that of Black salt, being composed of five endothermic peaks at 150, 170, 185, 230, and 290 °C. The apparent total weight-loss up to 350 °C in the TG curve is 52.3%, which is close to the value of 50.7%, calculated by assuming the final product to be cobalt(II) chloride. The gas-analytical data in Table 1 show that, on the pyrolysis of Red-I salt at 170 °C, only *ca.* 2 mol of ammonia are dissociated, accompanied by water of crystallization. However, pyrolysis at 220 °C causes the evolution of nitrogen and dinitrogen oxide besides ammonia and water. The compound obtained by pyrolyzing Red-I salt at 220 °C contained 27.2% of cobalt and 31.1% of chloride, and showed a magnetic susceptibility of 37.7 cgs. The apparent magnetic moment for the compound is, then, calculated as 4.4 B.M. on the basis of the cobalt content; it falls in the range of the magnetic moments of the high-spin-type Co(II) complexes.[10] By taking these observations into account, the DSC curve of Red-I salt may be interpreted as follows: the first endothermic peak, at 150 °C, corresponds mainly to the dehydration process; the second one, at 170 °C, to the elimination process of a part of the coordinated ammonia, and the third one, at 185 °C, to the decomposition of the coordinated hyponitrite group to dinitrogen oxide and the oxidation process of a coordinated ammonia to nitrogen, as will be discussed later.

Table 1. Analytical data of gaseous products evolved on pyrolysis

Complex	Temp/°C	N_2	N_2O	$NO^{a)}$	NH_3	$H_2O^{a)}$
		(Mol of evolved gas/mol of complex)				
Black salt	200	0.00	0.00	$1^{b)}$		
	290	0.07	0.00	$1^{b)}$	4.91	
Red-I salt	150	0.00	0.00	—	0.30	○
	170	0.00	0.00	—	1.81	○
	220	0.32	0.96	—		○
	290	0.39	0.96	—		○
Red-II salt	230	0.00	0.00	—		○
	310	2.70	0.21	—		○
$[Co(NH_3)_6]Cl_3$	310	0.17	0.00	—	4.66	
$[Co(NH_3)_5NO_2]Cl_2$	280	1.16	0.00	—	3.62	○

a) Since the calibration curves for these gases could not be obtained under the present experimental conditions, only qualitative data are given for NO and H_2O. Observation of the GC-peak due to H_2O is noted with ○; no observation of the GC-peak due to NO is noted with —. b) The apparent GC-peak of NO is ascribed to a quantitative elimination of NO, for the complex gives no, or only a minor quantity of N_2 and/or N_2O.

The DSC curve of Red-II salt shown in Fig. 1-c is composed of an endothermic peak with a maximum temperature at 230 °C and a large exothermic peak at

265°C, followed by a small endothermic peak at 280 °C. The weight-loss up to 350 °C in the TG curve is 71.0%. Miki and Ishimori[2] have reported, on the basis of the DTA data, that Red-II salt undergoes endothermic dehydration at 220 °C and then vigorous exothermic decomposition at 260 °C. The gas-analytical results shown in Table 1. reveal that only water is evolved on pyrolysis at 230 °C. The IR characteristic bands at 1480, 1280, and 1020 $\mathrm{cm^{-1}}$ assigned to the coordinated $(\text{-NO-ON-})^{2-}$ group were observed for the product obtained after pyrolyzing Red-II salt at 230 °C, but not for the product at 265 °C. Nitrogen, dinitrogen oxide, ammonia, and water were detected in the gaseous product evolved on the pyrolysis of this salt at 280 °C; ammonium chloride was also found to be produced. The pyrolysis at 350 °C resulted in leaving a mixture of cobalt(II) chloride and cobalt(III) oxide, which were identified by means of the IR spectrum.

Discussion

The experimental results are indicative of the following pyrolysis process of Black salt:

$$[\mathrm{Co^{III}(NH_3)_5NO}]\mathrm{Cl_2} \longrightarrow \mathrm{Co^{II}(NH_3)_2Cl_2} + (3\mathrm{NH_3} + \mathrm{NO})\uparrow$$

$$\mathrm{Co(NH_3)_2Cl_2} \longrightarrow \mathrm{Co(NH_3)Cl_2} + \mathrm{NH_3}\uparrow$$

$$\mathrm{Co(NH_3)Cl_2} \longrightarrow \mathrm{CoCl_2} + \mathrm{NH_3}\uparrow.$$

Black salt has been depicted formally as having the bonding unit Co(III)–$\mathrm{NO^-}$. Thus, the thermal decomposition in the first stage may be initiated by the electron transfer from the $\mathrm{NO^-}$ group to the central Co(III) ion, accompanied by the concomitant elimination of nitrogen monoxide and ammonia. Moreover, the sequence of dissociating ammonia is analogous with that of hexaamminecobalt(II) chloride, which subsequently gives diamminecobalt(II) chloride, monoamminecobalt(II) chloride, and finally cobalt(II) chloride, dissociating ammonia.[11]

Red-I salt includes a *cis*-hyponitrite group bridging two $\mathrm{Co(NH_3)_5}$ groups. As is shown in Table 1, the pyrolysis of Red-I salt at ⩾220 °C evolves nitrogen and dinitrogen oxide, besides ammonia and water; the total amount of the former two is more than one mole per mole of the complex. These facts indicate that the nitrogen in these two gases does not originate only from the hyponitrite group. Miki and Ishimori[2] have confirmed that the ammonia groups do not participate in the formation reaction of dinitrogen oxide, for the characteristic $^{14}\mathrm{N}^{15}\mathrm{NO}$ absorption is not observed in the IR spectrum of the gaseous product obtained by the pyrolysis of Red-I salt, which contains the ^{15}N-substituted hyponitrite group. The formation of nitrogen has not been taken into consideration.

In the investigations of pyrolytic behavior, it has been known that hexaamminecobalt(II) chloride decomposes liberating ammonia and gives cobalt(II) chloride,[11] whereas hexaamminecobalt(III) chloride decomposes in a different manner, depending on the conditions employed.[12–14] On the basis of the results obtained by means of the GEA method, where pyrolysis was carried out in a helium atmosphere and at a heating rate of 1 °C/min, Onodera[12] has recently demonstrated that the latter cobalt(III) complex produces nitrogen and ammonia, following a stoichiometric relation indicated by Eq. 1, which had been proposed by Clark *et al.*:[13]

$$[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3} \longrightarrow \mathrm{CoCl_2} + \mathrm{NH_4Cl} + 1/6\mathrm{N_2} + 28/6\mathrm{NH_2}. \quad (1)$$

However, the reaction mechanism forming nitrogen and/or ammonium chloride still remains obscure. Tanaka and Nagase[14] have pointed out the electron-transfer process involved in the reaction, and they determined, by means of a polarographic technique, the reduction rate of Co(III) to Co(II) on the pyrolysis reaction proceeding *in vacuo*, under isothermal conditions. For a series of the complexes, $[\mathrm{Co(NH_3)_{6-\mathit{n}}X_\mathit{n}}]\mathrm{X_{3-\mathit{n}}}$ (X=Cl or Br; n=0 or 1), the rates have been found to depend on the nature of X and on the number of n. The results have been interpreted in terms of the reductive behavior of the halide anion. As to the hexaammine complex, then, the following overall reaction has been presented:

$$[\mathrm{Co^{III}(NH_3)_6}]\mathrm{X_3} \longrightarrow \mathrm{CoX_2} + 6\mathrm{NH_3} + 1/2\mathrm{X_2}. \quad (2)$$

In order to verify nitrogen formation under the present experimental conditions, hexaamminecobalt(III) chloride has been analyzed by pyrolysis-gaschromatography. The results, shown in Table 1, indicate that the amounts of nitrogen and ammonia in the evolved gases are fairly consistent with the stoichiometric relation given in Eq. 1. It should be noticed that the amount of nitrogen is equivalent to that in the one-electron oxidation reaction of ammonia to nitrogen, with a change in the oxidation number from −3 to 0.

By taking the above evidence into consideration, the formation of nitrogen and dinitrogen oxide by Red-I salt can be explained as follows. After dehydrating and dissociating two moles of the coordinated ammonia, the complex is thermally induced to a transient state such as is shown in Eq. 3. Also, the dissociation of this transient species to $\mathrm{H^+}$ and $\mathrm{NH_2}$ species can be accelerated by a concomitant electron-transfer from the $\mathrm{NH_2^-}$ moiety to the cobalt(III) and by a subsequent nitrogen-forming reaction (Eq. 4) and dinitrogen oxide-forming reaction (Eq. 5).

$$[\mathrm{Co^{III}} - \mathrm{NH_2}] \longrightarrow \underset{\text{transient state}}{[\mathrm{Co^{III}} - \mathrm{NH_2^{\delta-}} \cdots \mathrm{H^{\delta+}}]} \longrightarrow$$

$$\mathrm{Co^{II}} + \mathrm{NH_2} + \mathrm{H^+} \quad (3)$$

$$\mathrm{NH_2} \longrightarrow 1/6\mathrm{N_2} + 2/3\mathrm{NH_3} \quad (4)$$

$$[\mathrm{H^+} \cdots \mathrm{O{-}N{=}N{-}O} \cdots\cdots \mathrm{H^+}] \longrightarrow \mathrm{N_2O} + \mathrm{H_2O} \quad (5)$$

The fact that an ammonia group in the hexaamminecobalt(III) cation readily exchanges the hydrogen atom with deuterium in a $\mathrm{D_2O}$ solution is not contrary to the above assumption.[15] The reduced cobalt(II) would release the bonding towards the hyponitrite group. Also, free hyponitrous acid is known to be thermally unstable, and it decomposes at −6 °C.[16]

On the pyrolysis of hexaamminecobalt(III) chloride, the proton expelled by Reaction 3 may be captured by ammonia and the chloride anion, thus forming thermally stable ammonium chloride.

The above assumption can well explain the facts that dinitrogen oxide, one mole per mole of Red-I salt, is produced exclusively from the coordinated hyponitrite group, and that nitrogen, 1/6 mol per mole of cobalt(III), is produced from a coordinated ammonia.

On the pyrolysis of Red-II salt, the nitrogen evolution is 8—9 times as much as that of Red-I salt. Moreover, the DSC curve in Fig. 1-c shows a large exothermic peak ascribable to the process forming nitrogen and dinitrogen oxide. The proposed structure of Red-II salt includes NO groups in a dimeric $(\text{-NO-ON-})^{2-}$ form, which implies an oxidative behavior of the peroxo moiety. This probably causes an unpredictable oxidation-reaction of ammonia other than that described above.

As for pentaamminenitrocobalt(III) chloride, the gas-analytical data shown in Table 1 are in good agreement with the stoichiometric relation in the following, overall reaction:

$$[\mathrm{Co(NH_3)_5NO_2}]\mathrm{Cl_2} \longrightarrow \mathrm{CoCl_2} + 7/6\mathrm{N_2} + 22/6\mathrm{NH_3} + 2\mathrm{H_2O}.$$

In this reaction, 1/6 mol of nitrogen can be attributed to the oxidation of the coordinated ammonia by the cobalt(III) ion, and one more mole to the following decomposition of ammonium nitrite, formed by the reaction of the H^+ in Eq. 3 and ammonia and the nitrite anion:

$$\mathrm{NH_4NO_2} \longrightarrow \mathrm{N_2} + 2\mathrm{H_2O}.$$

This nitrogen-forming reaction may be understood in terms of an oxidation of ammonia by the nitrite anion. This implies that the nitrogen evolution from Red-II salt would be attributable not only to Reaction 4, but also to an oxidation reaction of ammonia by the dimeric, $(\text{-NO-ON-})^{2-}$ group.

References

1) J. Sand and O. Genssler, *Ber.*, **36**, 2083 (1903).

2) E. Miki and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **49**, 987 (1976).

3) C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc., Inorg. Phys. Theor.*, **1971**, 2146.

4) B. F. Hoskins and F. D. Whillans, *J. Chem. Soc., Dalton Trans.*, **1973**, 607.

5) J. Bierrum and J. P. McReynold, *Inorg. Synth.*, **2**, 216 (1946).

6) S. M. Jorgensen, *Z. Anorg. Chem.*, **5**, 169 (1894).

7) T. Takeuchi and S. Tsuge, "Kobunshi no Netsubunkai-gaschromatography," Kagaku-Dojin, Kyoto (1977), pp. 47—54.

8) N. F. Curtis, *J. Chem. Soc.*, **1961**, 3147.

9) P. Gans, *J. Chem. Soc. Inorg. Phys. Theor.*, **1967**, 943.

10) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

11) W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 985 (1963).

12) S. Onodera, *Bull. Chem. Soc. Jpn.*, **50**, 123 (1977).

13) G. L. Clark, A. J. Quick, and W. D. Harkins, *J. Am. Chem. Soc.*, **42**, 2483 (1920); W. W. Wendlant, *J. Inorg. Nucl. Chem.*, **25**, 545 (1963); G. W. Watt, *Inorg. Chem.*, **3**, 325 (1964).

14) N. Tanaka and K. Nagase, *Bull. Chem. Soc. Jpn.*, **40**, 546 (1967); W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 1267 (1963).

15) J. S. Anderson, N. L. Spoor, and H. V. A. Briscoe, *J. Chem. Soc.*, **1943**, 361.

16) A. Hantzsch and L. Kaufman, *Lieb. Ann.*, **292**, 324 (1896).