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The Thermal Decomposition of Ammines of Cobalt(III) Chloride[1]

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The over-all reactions that occur during decomposition of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and *trans*-$[Co(NH_3)_4Cl_2]Cl$ to $CoCl_2$ *at high heating rates* are described; prominent features of the corresponding DTA and TGA curves are shown to be due to NH_4Cl volatilization. The decomposition of the hexaammine *at low heating rates* is shown first to provide the chloropentaammine followed by a sequence of phases that are described in terms of appropriate physical data.

Studies on the course of thermal decomposition of ammines of cobalt(III) chloride show that cobalt(II) chloride is formed as an intermediate and that it decomposes to the elements at higher temperatures.[2-10] Most of the available data and conclusions derive from differential thermal analyses (DTA) and/or thermogravimetric analyses (TGA) and their interpretation.

It is well established that the DTA curve for the decomposition of hexaamminecobalt(III) chloride, for example, exhibits two pronounced endothermal minima and that the TGA curve reveals two weight-loss processes that occur at different rates. There has been much speculation as to the significance of both major and minor features of such curves and more particularly about the identity of the precursors of cobalt(II) chloride. For the decomposition of $[Co(NH_3)_6]Cl_3$ to $CoCl_2$, for example, the following intermediate species have been postulated[2,4,8,9]: $[Co(NH_3)_5Cl]Cl_2$, *cis*- and *trans*-$[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_3Cl_3]$, $CoCl_2 \cdot NH_3 \cdot NH_4Cl$, $CoCl_2 \cdot NH_3$, and a possibly tetrahedral $Co(NH_3)Cl_3$. Since little unequivocal evidence has been advanced for each of these phases and since the conditions of decomposition including temperature have not always been the same in different studies, real questions on the nature of the process remain.

In the present work the thermal decomposition of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and *trans*-$[Co(NH_3)_4Cl_2]Cl$ was studied to (a) provide firm evidence on the stoichiometry of the over-all decomposition reactions, (b) determine whether these decompositions proceed through a common intermediate, (c) elucidate the significance of the DTA and TGA curves, and (d) determine whether or not it is in fact possible to establish the identity of at least some of the precursors of cobalt(II) chloride.

Experimental

Materials.—Hexaamminecobalt(III) chloride was prepared by the method of Bjerrum and McReynolds.[11] *Anal.* Calcd. for $[Co(NH_3)_6]Cl_3$: Co., 22.0. Found: Co, 21.6. Chloropentaamminecobalt(III) chloride was prepared as described by Willard and Hall.[12] *Anal.* Calcd. for $[Co(NH_3)_5Cl]Cl_2$: Co, 23.5. Found: Co, 22.9. *trans*-Dichlorotetraamminecobalt(III) chloride was prepared by a modification of the procedure of Werner and Klein.[13] *Anal.* Calcd. for $[Co(NH_3)_4Cl_2]Cl$: Co, 25.3. Found: Co, 25.0. For use in DTA experiments, chromatographic grade Al_2O_3 was washed with concentrated nitric acid, water, and alcohol and ignited at 1100° for 24 hr.

Method and Procedures.—DTA curves were obtained using a Model DS-2 apparatus manufactured by the Robert L. Stone Co., Austin, Texas. The heating rate was 8 ± 1°/min. All solids used were 120–230 mesh. Probably owing to the apppearance of both liquid and gaseous phases during the course of decomposition, poor reproducibility was experienced with the conventional procedure of mixing the reactant and alumina intimately in a 1:3 weight ratio. This difficulty was not encountered using the so-called micro method.[14] Curves were obtained using an atmosphere of flowing nitrogen (1 atm.) or an ammonia atmosphere at 3 atm.

TGA curves were obtained with a Chevenard thermobalance; samples were heated in static air and with nitrogen flowing at a rate of 1 l./min.; the heating rate was *ca.* 5°/min.[15]

Detailed studies of the reactions that occur at or near 300° were carried out as follows. A 500-ml. flask was fitted with a reflux condenser and charged with 150 g. of benzophenone which served as a heat transfer medium and was selected because of its appropriate boiling point of 306°. A Pyrex reaction tube was connected through the top of the flask with a ground glass joint so that the tube extended to within 3 in. of the bottom of the flask. The reaction tube was also fitted with inlet and outlet tubes to permit flushing with dry helium and was connected to a vacuum system having provisions for the collection and analysis of gaseous decomposition products. Weighed samples of the cobalt ammines were placed in the reaction tube, the flask was heated with a heating mantle, and the boiling benzophenone rapidly raised the temperature of the samples to the desired range. Upon completion of a reaction, the reaction tube containing an inert atmosphere was removed to a drybox for sampling and examination of solid products. The conditions otherwise employed are given below.

Experiments designed to detect intermediates in the decomposition of the hexaammine were carried out by heating *ca.* 250-mg. samples (contained in 4-mm. Pyrex tubes) in an efficiently stirred benzophenone bath at 0.5–1.0°/min. When the desired temperature was reached, the tubes were closed to prevent ingress

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[1] An earlier version of this manuscript was submitted on June 8, 1962, and subsequently withdrawn so that data from experiments involving low heating rates could be incorporated.

(2) W. Biltz, *Z. anorg. Chem.*, **83**, 177 (1913).

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(4) L. Kekedy, P. Kröbl, A. Szurkos, and E. Kekedy, *Acad. Rep. Populare Romine, Filiala Cluj, Studii Cercetari Chem.*, **9**, 79, 91 (1958).

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(6) W. W. Wendlandt, *Texas J. Sci.*, **10**, 271 (1958).

(7) M. Mori and R. Tsuchiya, *Bull. Chem. Soc. Japan*, **32**, 467 (1959).

(8) L. R. Ocone, J. R. Soulen, and B. P. Block, *J. Inorg. Nucl. Chem.*, **15**, 76 (1960).

(9) W. W. Wendlandt, *ibid.*, **25**, 545 (1963).

(10) W. W. Wendlandt and J. P. Smith, *ibid.*, **25**, 843 (1963).

(11) J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 217 (1946).

(12) H. H. Willard and D. Hall, *J. Am. Chem. Soc.*, **44**, 2220 (1922).

(13) A. Werner and A. Klein, *Z. anorg. allgem. Chem.*, **14**, 28 (1897).

(14) D. A. Vital, *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 2, 122 (1952).

(15) The writer is indebted to Dr. H. J. Borchardt, Explosives Department, E. I. du Pont de Nemours and Co., for these data.

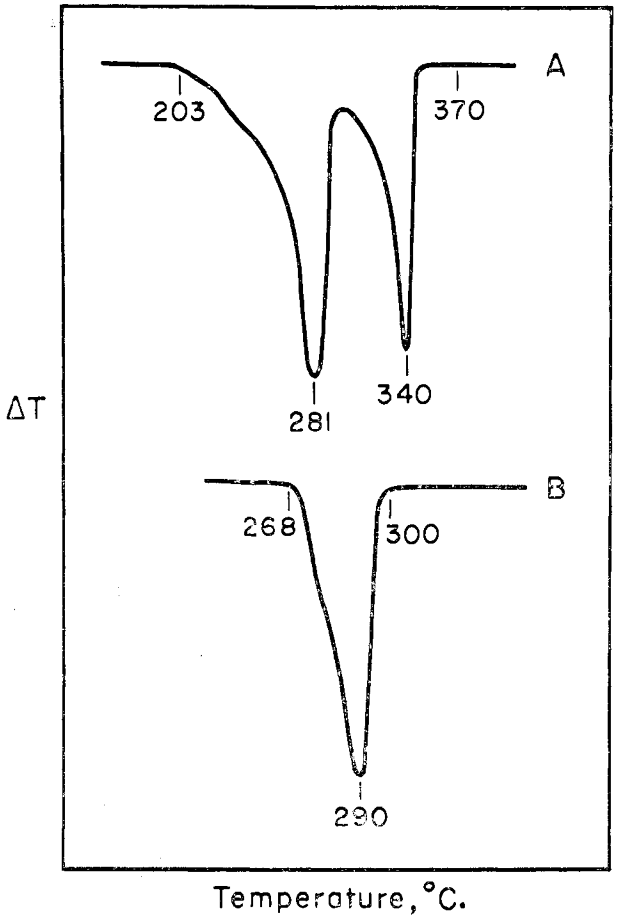

Fig. 1.—Differential thermal analysis curves for chloropentaamminecobalt(III) chloride: (A) in nitrogen (1 atm.), (B) in ammonia (3 atm.).

of air during quenching, and the tubes were quenched in a Dry Ice–isopropyl alcohol bath at $-75°$. It is estimated that the quenching time (*e.g.*, from 300 to $-75°$) was of the order of 1 sec. Thereafter the tubes were brought to room temperature and carefully protected from exposure to the atmosphere. The magnetic susceptibility of representative samples (<-200 mesh) was determined at 25° with a Curie–Cheneveau torsion balance,[16] and infrared spectra were obtained using a Beckman IR-7 instrument equipped with a long wave-length (CsI) interchange unit.

DTA Curves.—In 1 atm. of nitrogen, the decomposition of $[Co(NH_3)_5Cl]Cl_2$ exhibited two endothermal minima at 281 and 340°. In 3 atm. of ammonia, however, a single minimum at 290° resulted (Fig. 1).

The curves for the other two complexes were quite similar and are not reproduced here. That for $[Co(NH_3)_6]Cl_3$ in nitrogen showed a first departure from the base line at 222°, a very abrupt change in slope at 280°, a minimum at 294°, and return to base line at 310° followed by a second endothermal minimum at 341°. In ammonia, a single minimum at 300° resulted. *trans*-$[Co(NH_3)_4Cl_2]Cl$ in nitrogen similarly exhibited well-defined endothermal minima at 283 and 347°. In ammonia, these two did not quite coalesce to a single one but appeared as closely lying minima at 280 and 295°.

TGA Curves.—Data for the decomposition of the three ammines in flowing nitrogen are given in Fig. 2; since closely similar curves resulted when the decompositions were carried out in static air, they are not reproduced here. Taking $[Co(NH_3)_5Cl]Cl_2$ as a typical case, decomposition of a 0.1882-g. sample (Fig. 2) resulted in a measured weight loss of 0.089 g.; this is to be compared with 0.091 g. assuming that the final decomposition product was $CoCl_2$.

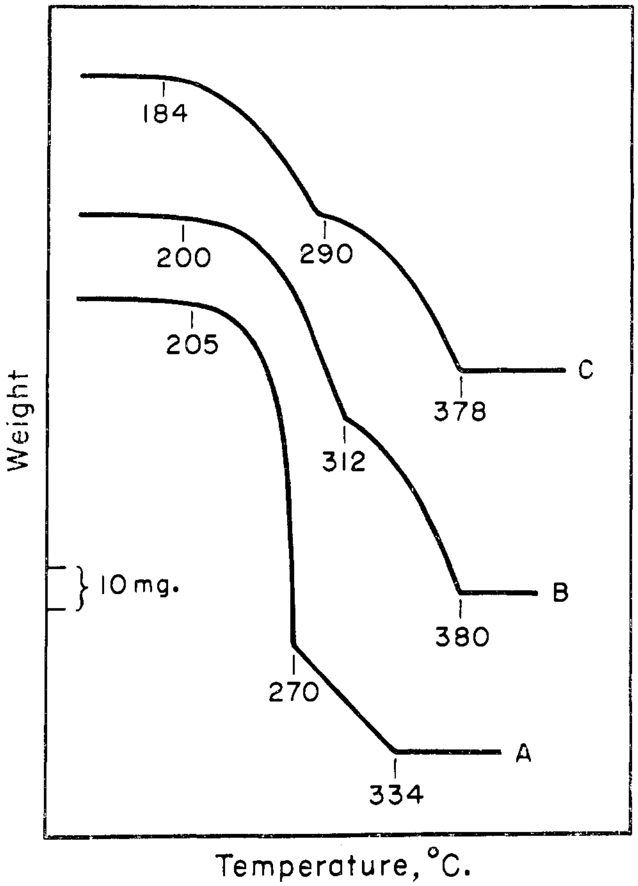

Fig. 2.—Thermogravimetric analysis curves for: (A) $[Co(NH_3)_6]Cl_3$, (B) $[Co(NH_3)_5Cl]Cl_2$, (C) $[Co(NH_3)_4Cl_2]Cl$.

Table I

Data on Gaseous Decomposition Products

Ammine	Moles of NH_3/mole of ammine	Moles of N_2/mole of ammine
$[Co(NH_3)_6]Cl_3$	4.66	0.18
$[Co(NH_3)_5Cl]Cl_2$	3.65	0.17
$[Co(NH_3)_4Cl_2]Cl$	2.67	0.17

Determination of Gaseous Products.—Using the reaction tube and procedures described above, weighed samples of the three complexes were decomposed by heating them to a maximum temperature of 306°, and the evolved gases were collected and analyzed (Table I). Mass spectrographic analyses showed the presence of only NH_3 and N_2 in addition to He sweep-gas.

To ensure that gas evolution was complete, separate samples of the three ammines were decomposed as described above, gaseous products were swept out with dry helium, and the residues were heated at 306° for an additional 1 hr. Further gas evolution did not occur.

Identification of Solid Products.—During the preceding decompositions, a white solid sublimed out of the reaction mixture just prior to melting, continued from the melt, and condensed near the top of the tube. This solid was removed in a drybox and gave an X-ray diffraction pattern identical with that for NH_4Cl. *Anal.* Calcd. for NH_4Cl: Cl, 66.4. Found: Cl, 66.8.

Upon exposure to air, the blue residue absorbed water and turned pink. This solid gave an X-ray diffraction pattern that showed only lines attributable to $CoCl_2 \cdot 6H_2O$ and NH_4Cl. In a separate experiment, the NH_4Cl was removed completely by vacuum sublimation and the resulting blue residue gave an X-ray diffraction pattern that corresponded exactly to that for $CoCl_2$.

Decomposition at Low Heating Rates.—Samples of the hexaammine were heated at 0.5–1.0°/min. to the temperatures listed

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[16] F. W. Gray and J. Farquharson, *J. Sci. Instr.*, **9**, 1 (1932).

TABLE II

DECOMPOSITION OF HEXAAMMINECOBALT(III) CHLORIDE

Product	Temp., °C.	Properties[a]
A	270	Pink solid
B	280	Red solid[b]
C	285	Lavender solid
D	287	Blue-lavender solid
E	289	Blue-gray solid
F	289–291[c]	Blue liquid
G	295	Blue liquid
H	300	Blue liquid

[a] Before quenching. [b] *Anal.* Calcd. for $[Co(NH_3)_5Cl]Cl_2$: Co, 23.5. Found: Co, 23.6. [c] Temperature range corresponding to maximum rate of water-insoluble gas evolution.

TABLE III

X-RAY DIFFRACTION DATA FOR COBALT(III) AMMINES AND DECOMPOSITION PRODUCTS OF HEXAAMMINECOBALT(III) CHLORIDE[a]

$[Co(NH_3)_6]Cl_3$[b]		$[Co(NH_3)_5Cl]Cl_2$[b]		*trans*-$[Co(NH_3)_4Cl_2]Cl$[c]	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
5.8	0.80	5.7	1.00	5.7	1.00
5.3	0.10	4.08	0.20	5.2	0.15
4.98	0.12	3.92	0.25	4.62	0.40
3.60	1.00	3.50	0.38	3.83	0.40
3.47	0.16	3.29	0.20	3.63	0.70
2.63	0.20	2.80	0.18	2.86	0.35
2.48	0.30	2.58	0.38	2.38	0.10[d]
2.05	0.12	2.04	0.20	2.13	0.20
2.02	0.10[d]	1.97	0.20[d]		

Product A		Product B		Product C		Product D	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
5.9	0.50	5.7	1.00	5.6	1.00	5.6	0.10
5.6	1.00	5.2	0.15	5.2	0.10	5.3	1.00
5.2	0.05	4.10	0.10	4.08	0.10	4.37	0.20
4.92	0.05	3.94	0.15	3.93	0.10	3.77	0.10[d]
4.07	0.05	3.49	0.40	3.50	0.30	3.49	0.15
3.98	0.05	2.79	0.30	3.30	0.05	3.01	0.25
3.59	0.60	2.59	0.40	2.77	0.15	2.77	0.30
3.47	0.50	1.97	0.10[d]	2.59	0.20		
2.78	0.05[d]			2.04	0.05		
2.58	0.15			1.97	0.05[d]		
2.45	0.10						

Product E		Product F		Product G		Product H	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
5.3	1.00	5.2	1.00	5.2	1.00	7.3	0.10
4.80	0.05	4.63	0.05	4.59	0.05	6.1	0.10
4.41	0.20	3.61	0.10	3.63	0.10	5.2	0.95
4.04	0.05	3.13	0.05	3.15	0.10	4.64	0.40
3.82	0.10	3.00	0.15	3.01	0.20	3.12	0.10[d]
3.67	0.05[d]	2.78	1.00	2.79	1.00	3.02	1.00
3.54	0.10	1.92	0.02	2.61	0.05[d]	2.79	1.00
3.06	0.15	1.88	0.02[d]	2.30	0.20	2.33	0.10
2.80	0.30					2.27	0.10[e]

[a] Patterns obtained using Cu Kα radiation, Ni filter, 40 kv. tube voltage, 15 ma. filament current, and 8–10 hr. exposure times; relative intensities estimated visually. [b] A.S.T.M. Index of X-Ray Diffraction Patterns. [c] This work. [d] Less intense lines not included here. [e] Essentially the same pattern was obtained when an independent sample was allowed to cool from 300 to 25° over 1 hr.

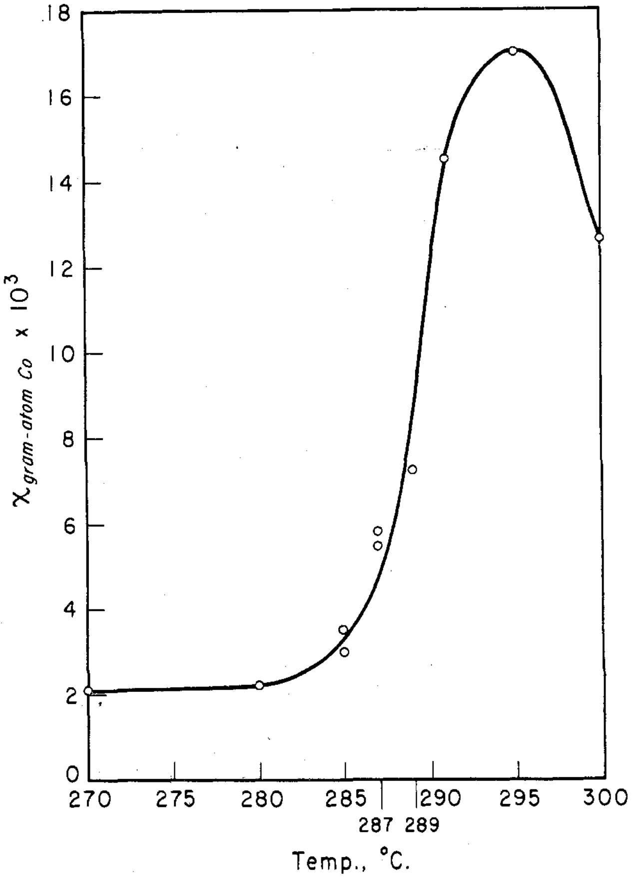

Fig. 3.—Magnetic susceptibility of decomposition products of hexaamminecobalt(III) chloride.

TABLE IV

INFRARED SPECTRAL DATA (CM.$^{-1}$) FOR DECOMPOSITION PRODUCTS OF HEXAAMMINECOBALT(III) CHLORIDE

Product B	Product E	Product H
284 vs	286 vs	. . .
. . .	310 vs	312 vs
330 vs	330 vs	. . .
. . .	. . .	430 vw, vb
467 w	467 vw	. . .
491 m	490 w	. . .
500 w	. . .	. . .
. . .	630 w, vb	631 s, vb

in Table II and immediately quenched as described above. The temperatures listed in Table II are those corresponding to visual evidence of change in color or phase. The resulting solids were ground in an inert atmosphere to ensure uniformity of composition, screened, and analyzed for cobalt. With a single exception (Table II) these analytical data did not correspond to any reasonable compositions and therefore were used only in relation to the data for Fig. 3.

X-Ray diffraction data for products A–H inclusive are given in Table III. Infrared spectral data (200–700 cm.$^{-1}$) for products B, E, and F are listed in Table IV.

When a sample of the hexaammine was heated under otherwise identical conditions but at a rate of 5–10°/min., clear melts (blue liquid) were obtained at temperatures that ranged from 298 to 301°.

Discussion

We consider first the decomposition of cobalt(III) ammines at heating rates hereafter referred to as "high," *i.e.*, the 5–10°/min. rates commonly used in TGA and DTA experiments. The results obtained in the present work (*e.g.*, Fig. 1 and 2) are generally in agreement with earlier data, and as earlier workers have suggested, most of the discrepancies that have been recorded seem to result from differences in heating rates together with obvious variables that influence heat transfer rates and volatile product removal. The importance of the former variable was clearly demonstrated in the present work on the decomposition of hexaamminecobalt(III) chloride: the minimum temperature of formation of a homogeneous liquid was increased about 10° by a five- to tenfold increase in heating rate.

Of more importance, however, is the fact that with one exception,[10] all the available TGA curves for ammine chlorides have the same general shape and all have a single feature in common, *i.e.*, a change in slope in the major weight loss regions of the curves. In Fig. 2, for example, this change occurs at 270, 312, and 290°. The corresponding temperatures taken from the curves obtained when the three ammines were decomposed in static air are 294, 313, and 294°. From Wendlandt's data[6] for the hexaammine and chloropentaammine it is estimated that this inflection occurs at 300 and 292°. Similar changes in slope appear in Block's curves in roughly the same temperature regions. Such changes in slope also appear in Wendlandt's data for $[Co(NH_3)_4(H_2O)Cl]Cl_2$, $[Co(NH_3)_5(NO_2)]Cl_2$, and $[Co(NH_3)_5(H_2O)]Cl_3$. Thus, this feature is common to all pyrolyses that could yield NH_4Cl as one of the products. It also seems significant that the temperatures listed above all fall in the region over which the vapor pressure of ammonium chloride[17] increases rapidly; the vapor pressures of NH_4Cl at 290, 300, and 310° are 189, 252, and 336 mm., respectively. In the pyrolysis of bromides, the change in slope should be either not observed or should occur at higher temperatures since the vapor pressure of ammonium bromide[18] is only 55 mm. at 300°. In two of three cases reported by Wendlandt, changes in slope are not observed; in the third case the observed changes could be due to other causes. Evidence is thus good that volatilization of NH_4Cl accounts for the relatively slow weight losses reflected by TGA curves and for the second endothermal minimum in the DTA curves (*e.g.*, Fig. 1) obtained using a flowing nitrogen or other inert gas atmosphere. When the ammines were decomposed under an ammonia pressure of 3 atm., NH_4Cl volatilization was suppressed and the single endothermal process observed (Fig. 1) corresponds to the total decomposition leading to $CoCl_2$.

As noted earlier, one TGA curve of Wendlandt and Smith[10] for the decomposition of $[Co(NH_3)_5Cl]Cl_2$ *in vacuo* showed no change in slope in the major weight loss regions of the curve. Wendlandt and Smith suggested that this fact might indicate that a different reaction mechanism was operative at atmospheric and reduced pressure. The arguments for volatilization of NH_4Cl suggested above indicate that rapid volatilization of NH_4Cl under reduced pressure would seriously alter the shape of the TGA curve just as observed.

The data in Table I and some earlier literature studies[3,9,10] show that the over-all reactions leading to the formation of $CoCl_2$ are

$$6[Co(NH_3)_6]Cl_3 \longrightarrow 6CoCl_2 + N_2 + 6NH_4Cl + 28NH_3 \quad (1)$$

$$6[Co(NH_3)_5Cl]Cl_2 \longrightarrow 6CoCl_2 + N_2 + 6NH_4Cl + 22NH_3 \quad (2)$$

$$6[Co(NH_3)_4Cl_2]Cl \longrightarrow 6CoCl_2 + N_2 + 6NH_4Cl + 16NH_3 \quad (3)$$

Thus, these reactions require a common mole ratio of nitrogen to parent ammine (1:6) and NH_3:ammine ratios of 14:3, 11:3, and 8:3; these are almost exactly the ratios computed from the data of Table I. Despite the striking similarity of behavior of these three ammines in DTA and TGA experiments, neither the present nor earlier studies provide evidence that they decompose *via* a common intermediate.

On the assumption that the heating rates typical of DTA and TGA experiments are too high to permit these techniques to be diagnostic with respect to the nature of the processes and species involved, the decomposition of one ammine was studied at a "low" heating rate, 0.5–1.0°/min. Hexaamminecobalt(III) chloride was selected because it is the ammine most extensively studied by earlier workers and about which there has been so much speculation as to mechanism of decomposition. Since this is a spin-paired complex, the rate of appearance of paramagnetic species can be attributed to either Co^{2+} formation or the removal of ligands to form spin-free Co^{3+}. Parallel X-ray diffraction and infrared spectral data (on the same samples) now make possible a detailed specification of the sequence of changes from $[Co(NH_3)_6]Cl_3$ to $CoCl_2$.

Up to 270°, the only significant change that occurs is loss of ammonia; the X-ray diffraction data of Table III (product A) show that the solid phase present at 270° is a mixture of hexaammine and chloropentaammine. At 280°, a conversion to the chloropentaammine is complete; this is established by analysis (Table II), X-ray diffraction data (Table III), and the infrared spectrum (Table IV). Figure 3 also shows that paramagnetic species are not present in appreciable concentration at this temperature. The spectral data are in good agreement with those of Shimanouchi and Nakagawa[19] and with a spectrum obtained independently in this laboratory.[20] Although the formation of the chloropentaammine by decomposition of the hexaammine has been a controversial question in the literature for many years,[2,4,5,8,9] the present data show that *at low heating rates* this product is formed substantially quantitatively. The present study, however, provided no evidence for the formation of either *cis*- or *trans*-dichlorotetraammine.

In the light of the foregoing results, the gas evolution data of Wendlandt at high heating rates are of

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[17] A. Smith and A. W. C. Menzies, *J. Am. Chem. Soc.*, **32**, 1448 (1910).

[18] A. Smith and R. P. Calvert, *ibid.*, **36**, 1363 (1914).

[19] T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).

[20] Although we find spectra for the three ammines that are closely similar to those of Shimanouchi and Nakagawa, we are not in complete agreement as to their interpretation. This will be the subject of a separate communication (G. W. Watt and D. S. Klett, unpublished work).

interest since he reports maximum rates of gas evolution at about 280° for the hexaammine[9] and about 290° for the chloropentaammine.[10] In the experiments that led to the results included in Table II, the maximum rate of gas evolution occurred at about 290°.

It is difficult to rationalize Wendlandt's rapid decomposition of hexaammine at 280° with any process which goes through a chloropentaammine since decomposition of the chloropentaammine is not rapid until 290° is reached.

X-Ray diffraction data for the phases present at 285 and 287° show clearly the persistence of the chloropentaammine and the appearance of other lines that cannot be attributed to any known compound of Co^{2+} or Co^{3+} for which X-ray data are available. This is the temperature range over which the rate of appearance of paramagnetic species begins to increase rapidly (Fig. 3).

The solid phase present at 289° (Table II, product E) is of particular interest since this corresponds to the temperature of incipient melting, and the onset of maximum rate of both gas evolution and generation of paramagnetic species. Although the X-ray data do not detect the chloropentaammine, weak but nevertheless characteristic infrared bands show that this species is still present at 289°, but at low concentration. The infrared bands at 310 and *ca.* 630 cm.$^{-1}$ show also the presence of Co^{2+} still bonded to NH_3 ligands. Based on the work of Quagliano, *et al.*,[21] these bands can be attributed to $[Co(NH_3)_6]Cl_2$ as such or partially deammoniated.

The solids resulting from the quenching of the liquids present at 289–291 and 295° give almost identical X-ray diffraction patterns that do not correspond to known cobalt compounds. These patterns, however, bear striking similarity to that for $(NH_4)_2ZnCl_4$,[22] but we do not suggest the presence of an isomorphous Co^{2+} analog because the infrared spectrum did not reveal the Co–Cl stretching frequency reported by Chatt and co-workers[23] for $CoCl_4^{2-}$. (The ammonium ion does not absorb in this region of the spectrum.[24]) It is therefore concluded that the X-ray patterns for these products are those of solid solutions of NH_4Cl and both Co^{2+} and Co^{3+} species, and that these solid solutions result from extremely rapid quenching of homogeneous melts containing randomly distributed ions. This is supported by the magnetic susceptibility data (Fig. 3), which show that Co^{3+} is necessarily present at both 291 and 295° since the measured moments are too high to be attributable to Co^{2+} alone.

The magnetic susceptibility of the solid corresponding to 300° is in good agreement with the value previously recorded[25] for $CoCl_2$. Thus, reduction to Co^{2+} is substantially complete at this temperature. Failure to detect $CoCl_2$ over the range 289–300° by either X-ray patterns or infrared spectra is attributed to the formation of solid solutions (*vide supra*). Cobalt(II) chloride was, however, identified as a product of both the present and earlier experiments employing high heating rates and flowing gas atmospheres; these are conditions more favorable to the removal of gaseous products. Finally, the infrared spectrum of the 300° product shows increased intensity of the two bands attributable to Co^{2+}–NH_3 species; this shows that metal ion–ligand bond rupture is not complete even at 300°. The final removal of these residual ligands could account for one of the minor gas evolution peaks observed by Wendlandt and Smith.[10]

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[21] E. P. Bertin, I. Nakagawa, S. Mizushima, T. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 525 (1958).

[22] A.S.T.M. Index of X-Ray Diffraction Patterns.

[23] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

[24] F. A. Miller, G. L. Carlson, F. F. Bentley, and W. H. Jones, *Spectrochim. Acta*, **16**, 135 (1960).

[25] N. Elliot, *J. Chem. Phys.*, **21**, 890 (1953).