ence is due to the fact that ν_5 is an almost pure M–O stretching vibration, whereas ν_4 and ν_{12} are more complex vibrations, which involve coupling between M–O stretching and other vibrations. By adjusting force constants of bonds other than the M–O and carbonyl groups, somewhat better agreement would probably be obtained. However, the results of the calculations illustrated in Table I are sufficient to show that ν_4 and ν_{12} are metal-sensitive and shift to higher frequencies as the M–O force constant increases. The nature of the bands which occur between ν_{12} and ν_5 in Fig. 1 is not obvious from the present calculations. It is seen, however, that these bands are also metal-sensitive. It is conceivable that they are derived from one of the out-of-plane ring vibrations, which were not treated in the present calculation.

In the region between 1600 and 1400 cm.$^{-1}$, more than three bands are observed in all the compounds studied. On the basis of the present calculations, the highest frequency band is assigned to the ν_3-vibration (ca. 75% C=C stretching plus 25% C=O stretching modes).[16] Since the main character of the bands is C=C stretching, the fact that their frequencies are the least sensitive of this group of bands to the nature of the metal is understandable. The second highest frequency band is assigned to ν_1-vibration (ca. 75% C=O stretching plus 25% C=C stretching) and is more sensitive to a change in the metal than ν_3-vibration. As is seen in Table I, two bands at 1545 and 1530 cm.$^{-1}$ in the Al(III) complex and at 1554 and 1534 cm.$^{-1}$ in the Cu(II) complex were tentatively assigned to the ν_1-vibration. The lowest frequency band is assigned to the ν_9-vibration (50% C=O stretching plus 50% C–H in-plane bending), although the calculated frequency is always higher than the observed values. This may be due to the fact that the C–H in-plane bending force constant is slightly

(16) The fact that the highest frequency band in this range is a C=C stretching and not a C=O stretching vibration would be difficult to predict on an empirical basis. However, this result is theoretically quite reasonable because: (1) the C=O bond orders are considerably lowered in the chelate ring and (2) the coupling between two relatively isolated C=O stretching modes is weak, whereas the coupling between two adjacent C=C stretching modes is relatively strong.

high. Since the ν_9-band is partly overlapped by a strong CH$_3$ degenerate deformation mode (1415 ~ 1390 cm.$^{-1}$), the band maxima are sometimes obscure.

Aluminum–Oxygen Bond.—Table I indicates that the band at 490 cm.$^{-1}$ in the Al(III) complex is an Al–O stretching band and the corresponding force constant is 2.60 × 10^5 dyne/cm. (Table II). This value is larger than that of the Cu–O bond which has partial double bond character. Thus we conclude that the Al–O bond is strongly covalent although different from the transition metals in that dπ–pπ bonding does not occur.

In order to confirm the band assignment, the infrared spectra of three Al(III) complexes of various β-diketones were compared. Since all three compounds (the 1:3 chelates of acetylacetone, benzoylacetone and dibenzoylmethane with Al (III)) exhibit absorptions between 490 and 450 cm.$^{-1}$ which do not exist in the free ligands, the assignments on the Al–O bonds are supported by these additional data. In this connection it should be noted that the band at 483 cm.$^{-1}$ in aluminum oxalate which was not assigned previously[5] now can be assigned to the Al–O stretching mode.

It was also observed that the Al–O stretching band shifts to lower frequency as the methyl group of acetylacetone is replaced by the phenyl group. As will be discussed in a subsequent publication the same band shifts to higher frequency by the same substitution in the case of transition metal chelates. It is conceivable that the resonance involving dπ–pπ bonding such as
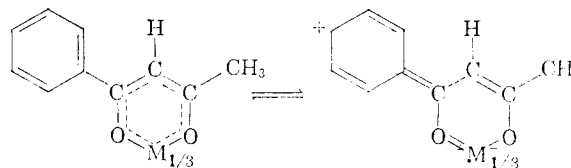
does not occur in the Al(III) complexes.

Products of the Thermal Decomposition of Some Cobalt Ammine Azides

BY TAYLOR B. JOYNER AND FRANK H. VERHOEK[1]

The thermal decompositions of solid [Co(NH$_3$)$_6$](N$_3$)$_3$, [Co(NH$_3$)$_5$N$_3$](N$_3$)$_2$, cis- and trans-[Co(NH$_3$)$_4$(N$_3$)$_2$]N$_3$ and Co-(NH$_3$)$_3$(N$_3$)$_3$ at 120 to 150° have been studied and the products characterized. The first four compounds behave similarly. Under varying conditions smooth reactions can yield N$_2$, NH$_3$ and CoN or Co(NH$_3$)$_2$(N$_3$)$_2$. Alternately explosions to Co, N$_2$, NH$_3$ and H$_2$ can occur. The triammine differs, exploding violently with no evidence of preliminary reactions.

Introduction

Recent reviews summarize the information available on the reactions of azide compounds.[2–4] In brief, two principal types of azides are most often

studied: covalent azides (i.e., HN$_3$, CH$_3$N$_3$) in which the azide group is associated with a single molecule and simple metal azides with the

(1) Ohio State University, Columbus, Ohio.

(2) W. E. Garner, "Chemistry of the Solid State," Butterworths Scientific Publications, London, 1955, Chap. 9.

(3) F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids," Academic Press, Inc., New York, N. Y., 1958.

(4) B. L. Evans, A. D. Yoffe and P. Gray, Chem. Revs., 59, 515 (1959).

azide ion occupying anionic sites in a salt-like lattice. The latter are often considered ionic, although a considerable degree of covalent character is recognized, particularly in the heavy-metal azides. The decomposition mechanisms differ. The covalent azides are thought to proceed by rupture of an N–N bond to give nitrogen and a radical RN, the metal azides by promotion of an electron to an exciton or conduction band leaving azide radicals, N_3, which react with each other to give nitrogen. The metal azides are particularly interesting because both inert compounds (alkali metal and alkaline earth azides) and very explosive heavy-metal azides (AgN_3, $Pb(N_3)_2$) exist.

Little attention has been paid to the decompositions of azide-containing coördination compounds of the transition metals. These are very attractive since one can make both covalent and ionic compounds with the metal-azide relationship clearly defined by the ligand sphere of the complex. Specifically, we have studied the series $[Co(NH_3)_6]$-$(N_3)_3$, $[Co(NH_3)_5N_3](N_3)_2$, cis- and trans-[Co-$(NH_3)_4(N_3)_2]N_3$ and $Co(NH_3)_3(N_3)_3$. These are well characterized, inner-orbital or strong field complexes[5] typical of the large number of cobalt-(III) coördination compounds. They are solids at ordinary temperatures with positive heats of formation[6] and highly exothermic decomposition reactions. Significantly, they possess two distinguishable types of azides. In the non-electrolyte $Co(NH_3)_3(N_3)_3$ the azides are closely associated with a particular cobalt atom. The bonding presumably has some covalent character. Alternately, in the ionic $[Co(NH_3)_6](N_3)_3$ the azides are isolated from the cobalt by the coördination sphere of ammonias, occupy sites in a salt-like lattice and presumably are similar to the anions in salts such as NaN_3.

This paper deals with the products and over-all stoichiometries of the thermal decompositions of the complex azides listed above. Although detailed discussion of the kinetics will be reserved for later papers, some descriptive material is included since both the kinetic behavior and resulting products differ depending on the experimental conditions.

Experimental

Preparation.—The cobalt(III) compounds were prepared and purified as previously described.[7,8] Powder samples of the hexammine were obtained by dissolving the crystalline compound in water and rapidly precipitating with a large excess of alcohol. Non-rotated X-ray powder patterns showed sharp lines. This and microscopic examination indicated average crystal diameters in the range of 10^{-4} to 10^{-2} mm. The samples were stored in vacuum desiccators over sulfuric acid and kept in the dark, although they were not protected from light during handling. Cobalt-(II) azide was prepared by the method of Wohler and Martin,[9] stored under a 3% solution of HN_3 in ether[10] and kept in the dark.

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chap. 2.

(6) T. M. Donovan, C. H. Shomate and T. B. Joyner, J. Phys. Chem., **64**, 378 (1960).

(7) M. Linhard and H. Flygare, Z. anorg. allgem. Chem., **262**, 328 (1950); M. Linhard, M. Weigel and H. Flygare, ibid., **263**, 233 (1950); M. Linhard and M. Weigel, ibid., **263**, 245 (1950).

(8) T. B. Joyner, D. S. Stewart and L. A. Burkardt, Anal. Chem., **30**, 194 (1958).

(9) L. Wohler and F. Martin, Ber., **50**, 586 (1917).

The compounds were identified by powder patterns[8] and titration of ionic azide with standard hydrochloric acid. Typical results are: Calcd. for $[Co(NH_3)_6](N_3)_3$, 43.9%. Found, powder, 43.9, crystals, 43.6. Calcd. for $[Co(NH_3)_5N_3](N_3)_2$, 31.1. Found, 30.8. Calcd. for $[Co(NH_3)_4(N_3)_2]N_3$, 16.6. Found, cis, 17.0, trans, 16.9.

The thermal decompositions also serve as fair analyses since total identification of nitrogen and hydrogen as N_2, NH_3 and H_2 was possible. The accuracy, generally within 5%, is within the limitations inherent in the apparatus and the use of 10-mg. samples. Greater inaccuracy noted in some runs, usually involving explosions, probably results from the scattering of partially decomposed material out of the hot zone.

Apparatus.—The decompositions were carried out in a vacuum system with a volume of 50 to 100 ml. depending on the particular reaction vessel used and some variations in the line during the course of the study. The usual vessel was cylindrical, about 20 cm. long, with an 8-mm. inner diameter, sealed at the bottom and capped with a standard-taper cap. It was attached to the vacuum line by a second standard-taper joint at right angles to its long axis. The vessel could be rotated around this second joint into a hot oil-bath controlled to $\pm 0.1°$. The glass vessel was reasonably well protected from the frequent explosions by placing the sample in a stainless steel cup 6 mm. in diameter and 6 mm. in depth. This was cushioned on a glass wool plug at the bottom of the vessel. A second plug above the cup limited rebound after one explosion hurled the cup against the top of the vessel with enough force to break the cap. A mercury manometer constructed of 2 mm. precision bore tubing measured gas pressures. Empirical corrections, obtained by measuring the pressure increases upon placing nitrogen samples in the hot bath, accounted for the volume of the system (ca. 10 ml.) at high temperatures.

Procedure.—A total of 80 runs have been made at temperatures of 120 to 150° and with the system initially evacuated or containing known amounts of ammonia, nitrogen or helium. In the usual procedure a weighed sample of explosive was placed in the reaction vessel, the system evacuated, and if desired a known quantity of gas admitted. The run was initiated by rotating the vessel into the oil-bath. The pressure increase with time was followed manometrically. Upon conclusion of the run the small reaction system could be opened to a more extensive line of traps and sample bulbs for the estimation of the gases. Generally this final estimation was made with the entire system at room temperature, and—when desired—the condensable (NH_3) and non-condensable (N_2, H_2) gases collected separately for mass spectrometric analysis. However, one of the solid products, $Co(NH_3)_2(N_3)_2$, absorbed ammonia upon cooling, complicating analysis. Usually the gas was sampled immediately after the run by closing off the still hot reaction vessel and taking the gas in the remainder of the line for mass spectrometric analysis without separating the condensable and non-condensable gases. While the point of major interest in these particular runs—the absence of hydrogen—was established clearly, the method was rather unsatisfactory for an accurate determination of nitrogen and ammonia. The difficulty arises in a diffusion problem, the gases sampled not being entirely representative of the system, and in some difficulty in the mass spectrometric determination of nitrogen to ammonia ratios at high concentrations of ammonia. Since the runs in question usually had added ammonia, the subtraction of the known added ammonia from the uncertain analytical data resulted in serious errors—up to 30%—in the estimation of the evolved ammonia.

The usual 10-mg. sample was too small for weight-loss studies desired to confirm the production of CoN. These were undertaken using the same apparatus but two ca. 60-mg. samples decomposed under non-explosive conditions. The results were within 10% of theory. The inaccuracy is attributable to errors in weighing small samples in a bulky reaction vessel subjected to excessive handling including the greasing and degreasing of standard-taper joints.

X-Ray Samples.—The decompositions produced three solids. Two of these, cobalt and CoN, are inert and may be handled in air. The cobalt results from explosions and was separated from a mixture of powdered glass and glass

(10) L. F. Audrieth and C. F. Gibbs in H. S. Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Company, New York, N. Y., 1939, p. 77.

wool by manipulation under the microscope. The cobalt (II) compound, $Co(NH_3)_2(N_3)_2$, was expected to be sensitive to oxidation and hydrolysis. Therefore, the reaction vessel's cap was replaced with one drawn to a tip upon which an 0.5-mm. diameter "Glaskapillaren" (made in West Berlin, Germany, available from Caine Scientific Sales Co., Chicago, Ill.) X-ray capillary was sealed with Apiezon W wax. After a run, the reaction vessel was inverted allowing the steel cup and sample to fall into the cap. Gentle tapping introduced a little sample into the capillary. This was sealed off with a small flame, mounted and the powder pattern taken. These operations frequently ended unsuccessfully in explosions. In actuality the compound is not overly sensitive to reasonably dry laboratory air since a sample loaded in the atmosphere gave a powder pattern identical with those loaded in vacuo. All X-ray photographs were taken with a 114.6-mm. diameter camera using CoK radiation filtered through an iron filter (λ = 1.7902 Å.).

Results

For the purpose of characterizing the products, the varieties of kinetic behavior observed and the final stoichiometries may be summarized by Fig.1. Here n/n_0 (moles of gas evolved per mole of compound) is plotted against time for a series of runs at 140°. Representative analytical data are reported in Table I. The reactions of $[Co(NH_3)_6]$-$(N_3)_3$ are quite typical and will be discussed specifically. Curves A, B and C illustrate the importance of the sample's crystal size and ammonia pressure. As would be expected, increasing temperature accelerates the reactions, shortens induction periods and makes more likely the explosion of the cobalt-(II) product, $Co(NH_3)_2(N_3)_2$ (curve B). In general, the predominant reactions are surprisingly well defined, although in a given run minor deviations from the expected stoichiometry may result from small quantities of the sample yielding one of the alternate products. It will be convenient to consider the reactions on the basis of the solid products.

TABLE I

PRODUCTS OF THE THERMAL DECOMPOSITION OF COBALT AMMINE AZIDES

Exp.	Compound	Initial NH₃ press., mm.	Temp., °C.	Gas evolved N₂	Gas evolved H₂	n/n_0 NH₃
1	$[Co(NH_3)_6](N_3)_3$	0	140.0	4.25	0.00	5.91
1a	CoN[a]	0	Flame	0.53	.02	0.04
2	$[Co(NH_3)_6](N_3)_3$ P[b]	213	140.2	2.52	.00	3.65
3	$[Co(NH_3)_6](N_3)_3$ P	46	140.2	1.22	.00	4.66
4	$[Co(NH_3)_6](N_3)_3$ P	196	139.9	1.51	.00	4.20
5	$[Co(NH_3)_6](N_3)_3$ P	0	120.2	1.01	.00	4.51
6E[c]	$[Co(NH_3)_6](N_3)_3$ P	0	140.1	5.50	2.85	4.17
7	$[Co(NH_3)_5N_3](N_3)_2$	0	140.0	4.04	0.00	4.93
7a	CoN	0	Flame	0.45[d]	..	0.06
8	$[Co(NH_3)_5N_3](N_3)_2$	0	140.3	3.73	0.00	4.70
8a	CoN	0	Flame	0.61	0.35	0.05
9E[c]	$[Co(NH_3)_5N_3](N_3)_2$	0	140.3	4.74	1.07	4.15
10E[c]	cis-$[Co(NH_3)_4(N_3)_2]N_3$	0	140.1	5.10	1.68	2.69
11E[c]	trans-$[Co(NH_3)_4(N_3)_2]N_3$	0	140.2	5.12	2.00	2.67
12E[c]	$Co(NH_3)_3(N_3)_3$	0	140.2	5.62	2.08	1.42

[a] Previous experiment is source of CoN. [b] P indicates powder. [c] E indicates an explosion. [d] No mass spectrometric analysis; the total non-condensable gas is reported as nitrogen.

Non-explosive Production of CoN.

—Crystalline $[Co(NH_3)_6](N_3)_3$ (crystals 0.05–0.5 mm. long), decomposed in the presence of its own products only, undergoes an induction period and a fast, non-explosive evolution of six moles of ammonia and four moles of nitrogen per mole of compound (Curve C, Exp. 1) to leave a black solid residue. This indicates the proportions of

$$[Co(NH_3)_6](N_3)_3 \longrightarrow CoN + 4N_2 + 6NH_3 \quad (1)$$
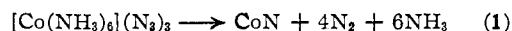
The solid was established as a nitride by heating in vacuo with a luminous flame to produce an additional 0.5 mole of nitrogen. Moreover, gravimetric studies on a 59.9 mg. sample revealed a residue weight of 25.7% after the initial decomposition and 21.2% after flaming. Calcd. for CoN 25.4% and Co, 20.5%.
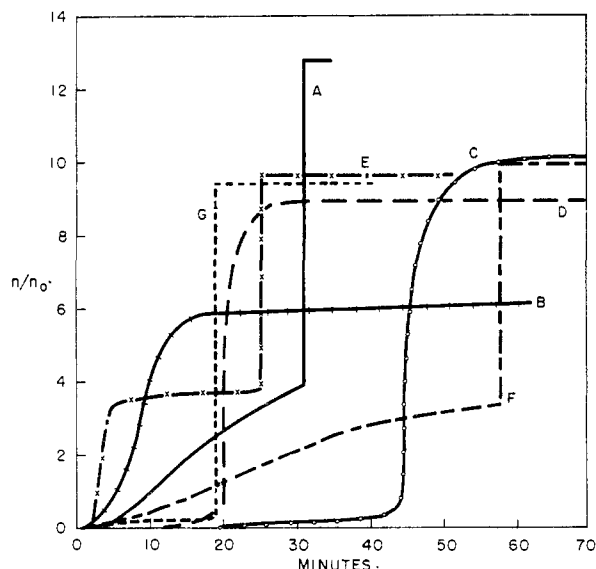

Fig. 1.—Thermal decomposition of cobalt ammine azides at 140°: A, $[Co(NH_3)_6](N_3)_3$, powder; B, $[Co(NH_3)_6]$-$(N_3)_3$, powder, 102.5 mm. NH₃ initially present; C, $[Co(NH_3)_6](N_3)_3$, crystals; D, $[Co(NH_3)_5N_3](N_3)_2$; E, cis-$[Co(NH_3)_4(N_3)_2]N_3$; F, trans-$[Co(NH_3)_4(N_3)_2]N_3$; G, $Co(NH_3)_3(N_3)_3$.

X-Ray powder patterns established the CoN as a compound with a cubic structure, a cell constant of 4.28 Å., and distinct from Co, Co₃N or Co₂N.[11] Schmitz–Dumont and Kron prepared a similar nitride by decomposing $Co(NH_2)_3$.[12] They found a cell constant of 4.27 Å. but report their structure as the sodium chloride type (no data are given) whereas a preliminary investigation of our line positions and intensities (Table II) suggests a zinc blende structure.[13] Thus, two modifications of CoN may exist. Powder patterns of the residue obtained by flaming our nitride revealed the expected metallic cobalt.

TABLE II

X-RAY POWDER PATTERN DATA FOR CoN

| d, (Å.)	Intensities (I/I_1)
2.48	1.00
2.14	0.33
1.51	.38
1.29	.22
1.24	.03
0.98	.06

(11) J. V. Smith, "Index to the X-ray Powder Data File," American Society for Testing Materials, Philadelphia, Pa., 1959, Alphabetical Section, p. 42.

(12) O. Schmitz-Dumont and N. Kron, Angew. Chemie, 67, 231 (1955).

(13) G. Palenik, private communication.

Hydrogen and ammonia are occasionally found in the gas evolved from the CoN and are thought to arise from small quantities of undecomposed starting material remaining in the residue. During flaming the $[Co(NH_3)_6](N_3)_3$ would yield large quantities of gas relative to the CoN. In the worst case encountered (exp. 8) about 5% of the starting material surviving in the CoN would account for the hydrogen, although there is some discrepancy in the nitrogen balance. Even in this extreme case, the hydrogen is insufficient to suggest a very attractive alternative to formulating the residue as CoN.

Non-explosive Production of Cobalt(II) Compounds.—Powdered $[Co(NH_3)_6][N_3]_3$ decomposed at 120 to 140° in the presence of excess ammonia (or occasionally at 120° in the presence of its own products only) undergoes a slow evolution of five to six moles of gas (Curve B) to leave a yellow or brown solid. Despite analytical difficulties caused by the solid's absorption of ammonia, mass spectrometric analysis revealed one to two moles of nitrogen, about four moles of ammonia and no hydrogen indicating a predominant reaction

$$[Co(NH_3)_6](N_3)_3 \longrightarrow$$
$$Co(NH_3)_2(N_3)_2 + 1.5 N_2 + 4NH_3 \quad (2)$$
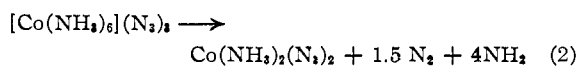
Since excess gas often is observed, side reactions such as decomposition by eq. 1 or complete loss of ammonia to cobalt(II) azide are likely. The quantities involved must be small since the deviation from eq. 2 is rarely over six moles of gas rather than the expected 5.5 and X-ray powder patterns show no $Co(N_3)_2$, CoN or Co lines. The patterns also eliminate any possibility that the yellow product is a mixture of orange starting material and black cobalt or cobalt nitride.

The yellow $Co(NH_3)_2(N_3)_2$ cooled in the presence of ammonia rapidly absorbs four ammonias per cobalt to yield a pink hexammine, $Co(NH_3)_6$-$(N_3)_2$. At room temperature this loses four ammonias to a liquid nitrogen trap within 4 hr. The remainder comes off slowly requiring more than two weeks. Above 110° the first four ammonias are lost within a minute whereupon an explosion occurs. This absorption and loss of ammonia is typical of cobalt(II) compounds.

Dry $Co(N_3)_2$ was also found to absorb ammonia with the production of pink compounds. X-Ray powder patterns taken to establish a definite link between the decomposition products and the Co-$(N_3)_2$-NH_3 compounds revealed a complicated system. The detailed experimental procedures and data will be reported separately. The points of interest to the present paper may be summarized briefly. The powder patterns established the decomposition products $Co(NH_3)_2(N_3)_2$ and $Co(NH_3)_6(N_3)_2$ as definite compounds. The Co-$(N_3)_2$-NH_3 system is complex apparently involving two diammines, both distinct from the "decomposition diammine," and a hexammine identical with that formed from the "decomposition diammine." Although some details of the system are still obscure, the identity of the hexammines links the decomposition products to the cobalt(II) azide system and with the stoichiometry of the de-

composition (Eq. 2) clearly establishes them as cobalt(II) compounds.

Explosive Production of Co.—Powdered [Co-$(NH_3)_6$] $(N_3)_3$ at 140° and in the presence of only its own products undergoes a slow evolution of 3 to 5 moles of gas followed by a violent explosion producing a total of about 12 moles of gas (Curve A, exp. 6) according to the approximate weight relationship of

$$[Co(NH_3)_6](N_3)_3 \longrightarrow Co + 5.5N_2 + 3H_2 + 4NH_3 \quad (3)$$
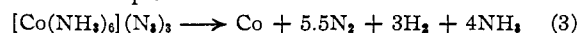
The ammonia destroyed may range from 0.5 to 2 moles with corresponding variations in the hydrogen and nitrogen observed. Powder patterns establish the residue as metallic cobalt.

$[Co(NH_3)_5N_3](N_3)_2$.—This compound closely resembles $[Co(NH_3)_6](N_3)_3$. Crystalline samples (crystals 0.05–0.1 mm. long) in the presence of their own products give CoN, four moles of nitrogen and five moles of ammonia non-explosively. Smaller crystals (0.01–0.02 mm.) resembled the powdered hexammine with an initial slow evolution of gas followed by an explosion (exp. 9). X-Ray powder patterns identified the products of the non-explosive and explosive runs as CoN and Co, respectively. Weight loss studies on a 59.8-mg. sample (exp. 7) strengthened the characterization of the nitride with residues of 28.3 and 24.2%. Calcd. to CoN, 27.0% and Co, 21.8%.

cis- and trans-$[Co(NH_3)_4(N_3)_2]N_3$.—Brief investigation has revealed only explosive behavior to cobalt, nitrogen, ammonia and hydrogen, although the decomposition curves clearly indicate breaks at $n/n_0 = 3.5$, the expected stoichiometry for the production of $Co(NH_3)_2(N_3)_2$. Efforts to sample the diammine for X-ray studies have been unsuccessful, although this certainly could be accomplished by further work.

$Co(NH_3)_3(N_3)_3$.—Little work has been done with this highly explosive compound. It differs from the other members of the series in that only very small quantities of gas are evolved prior to the violent explosion to cobalt, nitrogen, hydrogen and ammonia.

Discussion

It is interesting that under various conditions $[Co(NH_3)_6](N_3)_3$ can show different kinetic behavior leading to three distinct sets of products. The cobalt(II) compound, $Co(NH_3)_2(N_3)_2$ resulting from a one-electron reduction of the cobalt(III) complex by an azide ion is probably being built up during the initial period of the decomposition of the powdered compound and is very likely responsible for the final explosion. It may also be an intermediate in the smooth decomposition to CoN, although in this case its accumulation would be prevented by rapid reaction to the final product. CoN is not an explosion product. Even if momentarily formed, its lability is such that it would not be expected to survive the extreme conditions of an explosion. Of the remaining compounds, the pentammine closely resembles the hexammine, the tetrammine are similar in apparently yielding $Co(NH_3)_2(N_3)_2$ followed by an explosion, although the non-explosive reaction to CoN has not yet been observed, while the triammine behaves quite differently from the rest of the series.