TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[N(CH_3)_4]_2B_6H_6$

h	k	ℓ	$K\lvert F_o\rvert$	F_c
0	0	2	92	-95
0	0	4	32	30
0	0	6	48	48
0	0	8	15	15
0	0	10	12	12
0	2	2	136	140
0	2	4	6	5
0	2	6	4	-3
0	2	8	11	11
0	2	10	21	22
0	4	4	12	11
0	4	6	27	-26
0	4	8	20	21
0	4	10	5	-4
0	6	6	28	29
0	6	8	20	-20
0	8	8	23	22
1	1	1	75	73
1	1	3	58	58
1	1	5	0	1
1	1	7	14	15
1	1	9	19	19
1	1	11	7	10
1	3	3	48	-46
1	3	5	16	15
1	3	7	0	-2
1	3	9	0	4
1	5	5	20	-19
1	5	7	6	-5
1	5	9	10	9
1	7	7	5	3
2	2	2	53	-54
2	2	4	8	9
2	2	6	10	-8
2	2	8	10	12
2	2	10	0	0
2	4	4	47	-47
2	4	6	11	9
2	4	8	17	-17
2	4	10	13	12
2	6	6	33	-35
2	6	8	16	15
3	3	3	51	51
3	3	5	60	-58
3	3	7	8	-9
3	3	9	12	12
3	5	5	4	-3
3	5	7	8	-8
3	5	9	10	-11
3	7	7	8	-11
4	4	4	8	6
4	4	6	38	-38
4	4	8	0	1
4	6	6	5	-5
4	6	8	11	-10
5	5	5	29	-28
5	5	7	17	-16
5	7	7	7	-4
6	6	6	11	-11

TABLE III

BOND DISTANCES IN $[N(CH_3)_4]_2B_6H_6$

B–B	1.69 ± 0.01 Å.
B–H	1.11 ± 0.07 Å.
C–N	1.48 ± 0.01 Å.
C–H	0.99 ± 0.04 Å.

Comments.—Study of the behavior of a small sample of $[N(CH_3)_4]_2B_6H_6$ in a micro-differential calorimeter showed only a weak endothermic change between 405 and 407°K. After cooling to room temperature for 30 min., a second warming period did not reproduce the endothermic change. The observed transition might correspond to conversion of the methyl group to a freely rotating state, but further studies should be carried out.

Acknowledgments.—We wish to express our thanks to Dr. J. Boone for samples and permission to carry out this study, and to Mr. V. Silveira for the powder photography. This work was performed under the auspices of the U. S. Atomic Energy Commission.

CONTRIBUTION FROM THE U. S. NAVAL
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Azide Salts of *trans*-Diazidotetraamminecobalt(III) Ion

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In the course of studies with *trans*-diazidotetraamminecobalt(III) azide a second crystal form of the compound and a double salt with sodium azide were identified by their powder patterns. Since the appearances in both the solid state and aqueous solution are similar and the inadvertent preparation of the new compounds easy, a report on this possible source of confusion seems desirable.

Experimental

Preparation.—The complex is prepared by Linhard's method.[1] In brief, the double salt precipitates from an aqueous solution saturated with sodium azide, the usual compound (designated form I, the powder pattern has been reported[2]) from solutions one-third or less saturated with sodium azide,[1] and the crystal modification (form II) occasionally results from the rapid precipitation of aqueous solutions of form I with ethanol and ether. The interconvertibility of the three compounds is demonstrated by the following preparations.

(A) ***trans*-$[Co(NH_3)_4(N_3)_2]N_3 \cdot NaN_3$ and *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (Form I).**—Eight grams of freshly prepared $[Co(NH_3)_4(H_2O)_2]Cl_3$ treated according to Linhard[1] yielded 3.2 g. of crude *trans*-$[Co(NH_3)_4(N_3)_2]N_3$. This was dissolved in 70 ml. of water at 23°, filtered, precipitated by saturating with sodium azide, and washed with three 5-ml. portions of ethanol followed by ether; yield 2.4 g., designated **1**. Two grams of 1 precipitated according to Linhard[1] (solution in 48 ml. of water at 40° and precipitation with 24 ml. of saturated aqueous sodium azide at 5°) yields 1.4 g., designated **2**. A 0.5-g. sample of **2** dissolved in 22 ml. of water, filtered, and precipitated by saturating with sodium azide yields 0.5 g., designated **3**. Samples 1 and **3** had the powder pattern of the double salt (Figure 1, pattern C) while **2** was the usual *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (form I) (Figure 1, pattern A). All three are crystalline, dark blue to the eye, and reddish brown plates under the microscope.

(B) ***trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (Form II).**—Rapid precipitation of aqueous solutions of form I with ethanol and ether produced brown powders. Unexpectedly, the first preparation showed a distinct powder pattern (Figure 1, pattern B). Later efforts to obtain the new material usually failed (yielding only form I). To the present, four of fifteen efforts have succeeded. While the conditions for the preparation of form II are still not clear, it appears that temperature and the proportions and rate of mixing of the reagents are important. Inadvertent seeding by microscopic nuclei of one form or the other may also contribute to the unpredictability of the reprecipitations. A successful preparation used 0.19 g. of form I dissolved in 22 ml. of water, which was filtered and precipitated with 200 ml. of ethanol followed by four 50-ml. and one 300-ml. portions of ether added with stirring. The temperature was maintained at 28 to 30°; yield 0.14 g.

Once obtained, form II may be reconverted to form I in *ca.* 80% yield by recrystallization according to Linhard[1] or, with more difficulty, by reprecipitation with ethanol and ether. This reluctance to reprecipitate as form I is indicated by the following: four reprecipitations of *ca.* 5-mg. samples yielded only form II, one 5-mg. experiment gave a mixture of I and II, and one of four essentially identical experiments with 25-mg. samples yielded form I. The last used 25 mg. of form II dissolved in 1 ml. of water at 22° and precipitated by the slow (*ca.* 10-min.) addition of 40 ml. of a 1:3 ethanol–ether solution. The yield of form I was greater than 18 mg.

Analysis.—Ionic azide was precipitated as silver azide, washed with ethanol, dried at room temperature, and weighed. Several analyses were checked by solution of the silver azide in nitric acid and precipitation and oven drying of silver chloride. Cobalt was determined gravimetrically as the anthranilate[3] following

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[1] M. Linhard, M. Weigel, and H. Flygare, *Z. anorg. allgem. Chem.*, **263**, 233 (1950).

[2] T. B. Joyner, D. S. Steward, and L. A. Burkardt, *Anal. Chem.*, **30**, 194 (1958).

[3] P. Wenger, C. Cimerman, and A. Corbaz, *Mikrochim. Acta*, **2**, 314 (1938).

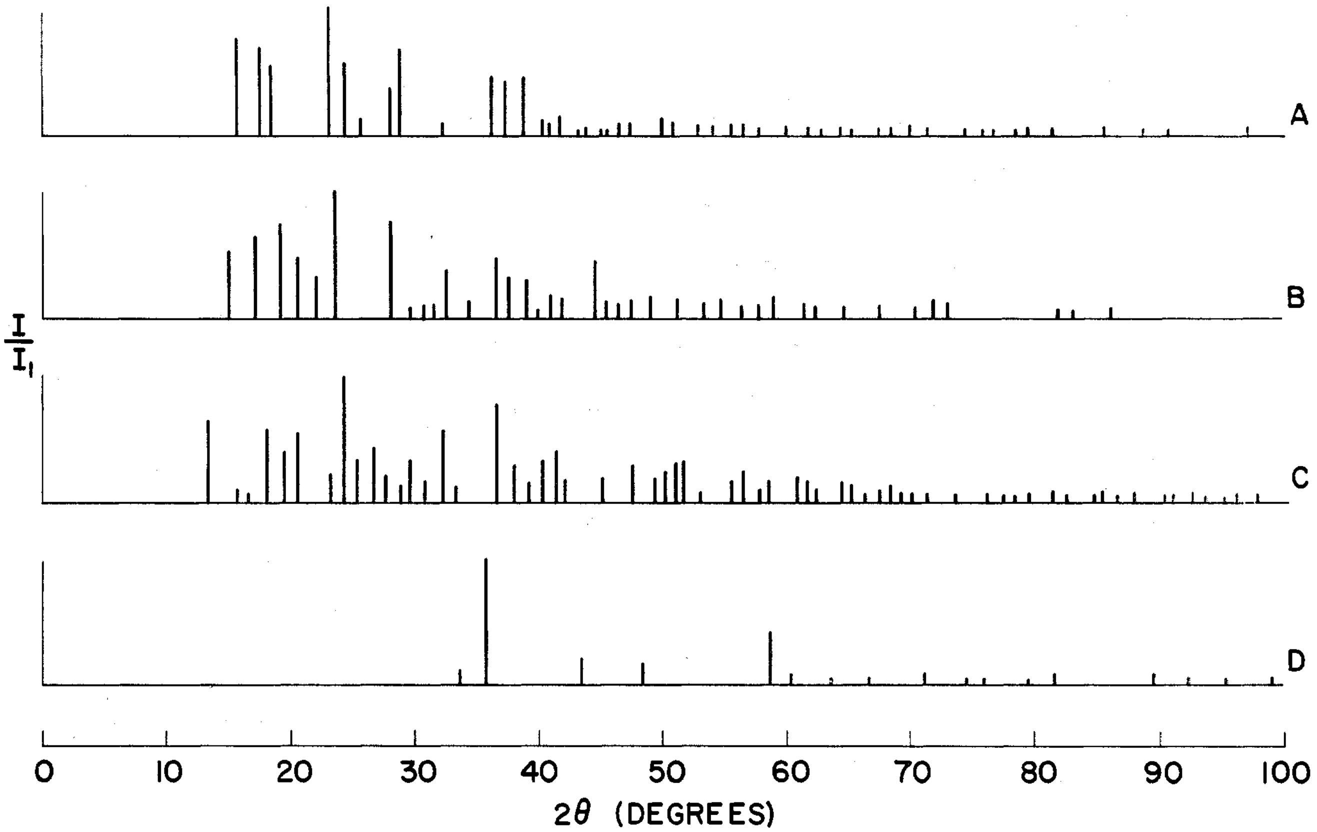

Figure 1.—Powder patterns: A, *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (form I); B, *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (form II); C, *trans*-$[Co(NH_3)_4(N_3)_2]$-$N_3 \cdot NaN_3$; D, NaN_3, Hanawalt, Rinn, and Frevel.[6]

destruction of the complex by evaporation to dryness with concentrated sulfuric acid. The absence of chloride (possibly carried over from $[Co(NH_3)_4(H_2O)_2]Cl_3$) was checked with silver nitrate in a hot nitric acid solution of the complex.

(A) **Double Salt.**—*Anal.* Calcd. for $[Co(NH_3)_4(N_3)_2]$-$N_3 \cdot NaN_3$: Co, 18.5; ionic N_3^-, 26.4. Found: Co, 18.9; ionic N_3^-, 26.4.

Efforts to determine the total azide following basic hydrolysis of the complex established the presence of coordinated azide but yielded values of 40.0 and 46.0; calcd. 52.8. The discrepancy probably results from some oxidation of the azide during hydrolysis. Sodium was detected qualitatively by evaporating to near dryness with concentrated hydrochloric acid and extracting the cobalt(II) chloride with ethanol. A powder pattern identified the residue as sodium chloride and ammonium chloride.

(B) **Simple Azides.**—*Anal.* Calcd. for $[Co(NH_3)_4(N_3)_2]N_3$: Co, 23.3; ionic N_3^-, 16.6. Found (form I): Co, 23.2; ionic N_3^-, 16.8. Found (form II): Co, 23.6 (23.6); ionic N_3^-, 16.7 (17.2).

The values in parentheses were given by the original sample after 2 years storage in a vacuum desiccator. Powder patterns showed no change during this period; however, some water-insoluble contaminant—possibly foreign material—had accumulated. In the analysis this was filtered out, weighed, and allowed for in the calculations.

Absorption Spectra.—The presence of the *trans*-$[Co(NH_3)_4(N_3)_2]^+$ ion in all three compounds is indicated by the typical blue (or blue-red) color of aqueous solutions. Quantitative confirmation and support for the formulation of the double salt is provided by absorption spectra taken with a Cary Model 11 spectrophotometer. All three spectra are essentially identical and in good agreement with Linhard and Weigel regarding the position and extinction coefficients of the two peaks.[4] A shoulder at 215 mμ is somewhat enhanced for the double salt relative to the simple compounds (molar extinction coefficients of 15.7×10^3 and 14.2×10^3, respectively) as a result of absorption by the sodium azide.[5]

X-Ray Powder Patterns.—Film patterns were recorded in a 114.6-mm. diameter camera using Co K radiation filtered through an iron filter (λ 1.7902 Å.). Samples were rotated. Line intensities were taken as peak height above the background level of densitometer tracings. The results are summarized in Figure 1 with the pattern of sodium azide[6] included for comparison. The clear distinction of the compounds is evident. The data have been filed with the A.S.T.M. X-Ray Powder Data File. In the case of *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (form I) a previously reported[2] weak line at $d = 7.67$ ($2\theta = 13.40$) is not observed here. It presumably resulted from the presence of a small amount of double salt in the previous sample.

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[4] M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **267**, 121 (1951).

[5] H. Mohler, *Helv. Chim. Acta*, **26**, 121 (1943).

[6] J. D. Hanawalt, H. W. Rinn, and L. K. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
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Reaction of Trichlorophosphonitridosulfuryl Chloride with Hydrofluoric Acid. Amidosulfuryl Fluoride

BY LUDWIG K. HUBER AND HARRY C. MANDELL, JR.

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The preparation of amidosulfuryl fluoride has been reported recently. Appel and Senkpiel[1] obtained the

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[1] R. Appel and W. Senkpiel, *Angew. Chem.*, **70**, 572 (1958).