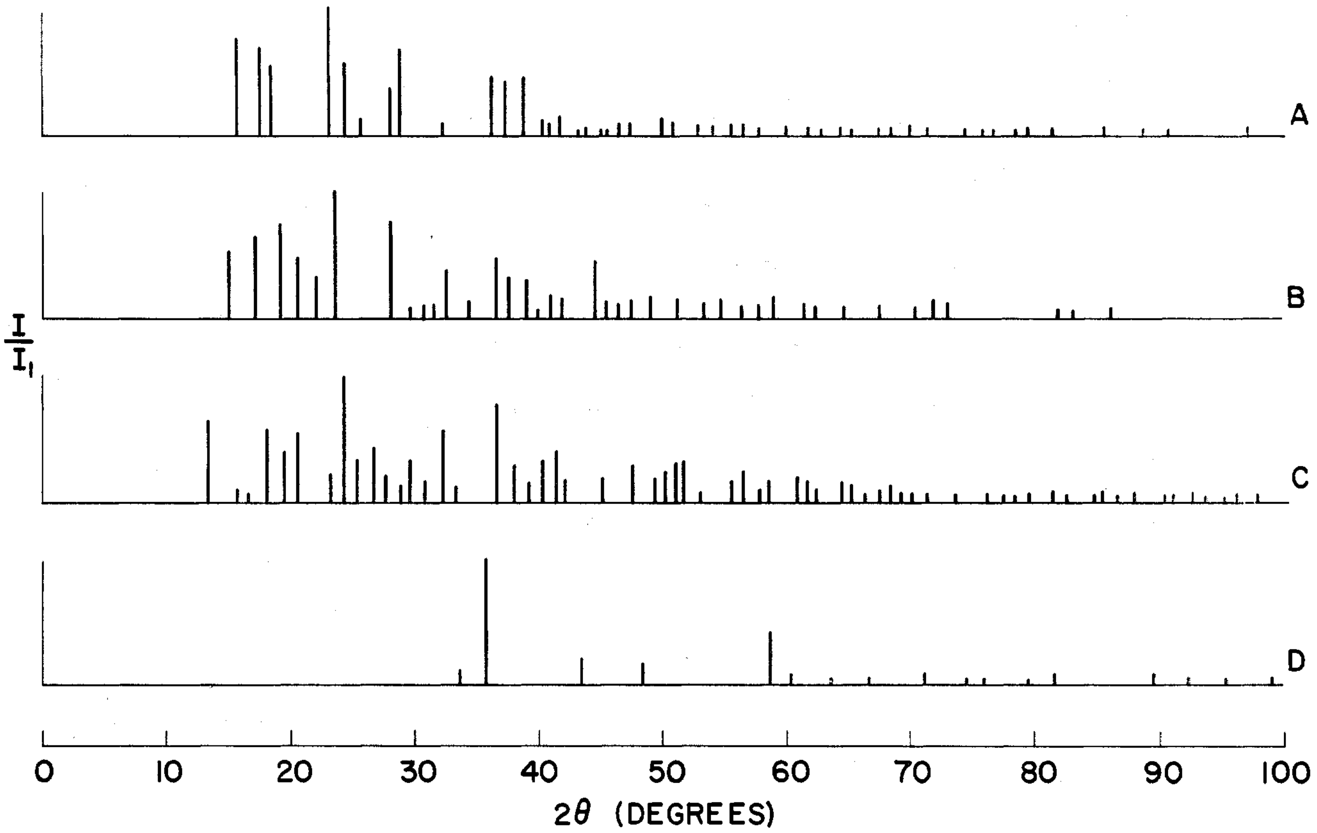

Figure 1.—Powder patterns: A, *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (form I); B, *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (form II); C, *trans*-$[Co(NH_3)_4(N_3)_2]$-$N_3 \cdot NaN_3$; D, NaN_3, Hanawalt, Rinn, and Frevel.[6]

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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Reaction of Trichlorophosphonitridosulfuryl Chloride with Hydrofluoric Acid. Amidosulfuryl Fluoride

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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).

compound by the reaction of amidosulfuryl chloride and an alkali fluoride; Jonas and Voigt[2] allowed isocyanatosulfuryl chloride to react with an alkali fluoride to form isocyanatosulfuryl fluoride, which subsequently was hydrolyzed to amidosulfuryl fluoride. No yields have been reported on these methods, both of which require several steps to prepare the compound from commercially available products. In another route published by Appel and Eisenhauer[3] amidosulfuryl fluoride is said to be made by ammonolysis of disulfuryl fluoride. Again several additional steps or a pressure reaction are involved to prepare the very toxic intermediate in good yields.

We wish to report a new reaction which permits production of amidosulfuryl fluoride with high over-all yields by a simple two-step reaction from available materials. First sulfamic acid is allowed to react with phosphorus pentachloride to form the known trichlorophosphonitridosulfuryl chloride[4] (yields up to 95%). When treated with liquid anhydrous hydrofluoric acid, trichlorophosphonitridosulfuryl chloride undergoes reaction by which the P=N bond is cleaved. At the same time at least some of the chlorine atoms are substituted by fluorine, and amidosulfuryl fluoride is formed according to the reaction

$$Cl_3PNSO_2Cl + xHF \xrightarrow{BF_3} H_2NSO_2F + P(Cl,F)_5 + nHCl \qquad n = 1\text{–}4$$

Addition of some boron trifluoride is necessary to promote the reaction, suggesting a proton-catalyzed mechanism.

Amidosulfuryl fluoride is produced in yields up to about 70–75% and can be isolated in essentially pure form simply by distillation. Purer product is obtained by extraction of the reaction mixture with suitable organic solvents prior to distillation.

Attempts to prepare amidosulfuryl fluoride by reaction of trichlorophosphonitridosulfuryl chloride with anhydrous hydrofluoric acid alone, or by heating it with alkali fluorides in acetonitrile, did not produce the desired product.

Amidosulfuryl fluoride has been found to be sufficiently stable to be stored in glass containers for extended periods of time, if moisture is thoroughly excluded.

Experimental

Trichlorophosphonitridosulfuryl chloride (27 g., 0.108 mole), made by the method of Kirsanov,[4] was placed in a Teflon trap and about 30 ml. of anhydrous hydrofluoric acid and about 2–3 g. of boron trifluoride were condensed upon it. (A convenient way to liquefy hydrofluoric acid is to pass the gas through an ice-cooled copper coil.) The clear colorless solution formed was left at room temperature for 2.5 days protected from moisture. During this time there was evaporation of part of the hydrofluoric acid, together with hydrochloric acid and phosphorus halogenides produced as by-products. The rest of the low-boiling material (mainly HF) was stripped off at room temperature and about 5 mm. pressure. The residue was distilled in a small glass apparatus at reduced pressure to yield 8 g. (74% of theory) of crude product which melted at 5°. On redistillation at 3 mm. pressure the product distilled constantly at 70° (lit. b.p. 88° (12 mm.)) and melted at 6° (lit. m.p. 7–8°).

Anal. Calcd. for H_2FNO_2S: N, 14.1; S, 32.3; F, 19.1. Found: N, 13.2; S, 31.9; F, 18.3.

A pure sample of amidosulfuryl fluoride was obtained by washing crude reaction product first with benzene and subsequently extracting amidosulfuryl fluoride with chloroform prior to distillation. The sample so purified melted at 6–8°.

Anal. Calcd. for H_2FNO_2S: N, 14.1. Found: N, 14.1.

The compound has the following infrared absorption bands (cm.$^{-1}$): 3401 (s), 3311 (s), 1553 (m), 1410 (vs), 962 (m), 784 (vs).

Acknowledgment.—Analytical work was performed by our Analytical Department, including the interpretation of the infrared spectra by Miss Ruth A. Kossatz.

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The Preparation and Structure of Anhydrous Bis(dipivaloylmethanido)iron(II)

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Studies of the physical properties of solvated and unsolvated β-diketone complexes of iron(II) are usually troubled[2] by the reactivity of the species with oxygen. Recent studies by Buckingham, *et al.*,[3] have shown that bis(2,4-pentanediono)iron(II) is high-spin (μ = 5.4 B.M. at room temperature) and has a limited room-temperature solubility (~1–2% w./v.) in nonpolar organic solvents such as benzene or toluene. It appears that the anhydrous $Fe(acac)_2$ exists as a weakly associated polymer in the solid state and in solution. Polymerization has been found previously with $Ni(acac)_2$,[4] $Co(acac)_2$[5,6] and $Mn(acac)_2$.[7]

With 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane) as the β-diketone, polymerization is prevented[8] and one forces the metal to assume a coordination number of four (or less) in the neutral bis complex. In the case of nickel(II) and copper(II), a planar molecule results, while with cobalt(II) and

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[1] (a) Case Institute of Technology; (b) Brown University.

[2] See, for example, D. A. Buckingham, J. L. E. Cheong, J. E. Fergusson, and C. J. Wilkins, *J. Chem. Soc.*, 3461 (1963). G. S. Hammond, D. C. Nonhebel, and C-H. S. Wu, *Inorg. Chem.*, **2**, 73 (1963), report an unsuccessful attempt to prepare $Fe(DPM)_2$.

[3] D. A. Buckingham and J. T. Henry, to be published.

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