Hence, the latter should be more easily formed by dehydrating gibbsite (specific gravity of 2.43), since dehydration would certainly lead to an open structure.

On the basis of this investigation it is possible to construct a tentative solubility curve for the system alumina–water. Figure 2 shows the solubility in water of the stable phases of the alumina–water system as a function of temperature. Quantitative data for the solubilities have not been obtained but we know qualitatively that the solubility curves should show discontinuities at the various transition points and should indicate greater solubility at higher temperatures, and that the stable phases should be less soluble than the metastable phases.

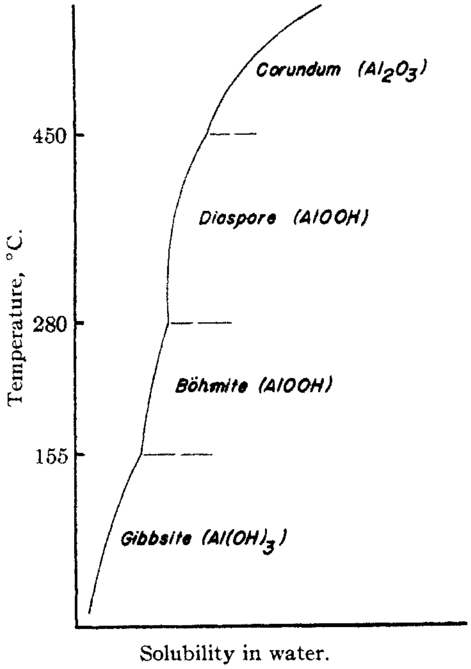

Fig. 2.—Solubility curves for the system alumina–water.

The authors wish to thank Prof. C. C. Murdock who made available X-ray diffraction apparatus, and Prof. C. W. Mason who furnished microscopical equipment.

Summary

1. The system alumina–water has been studied by the hydrothermal method in the temperature range 100–500°. The phases involved were identified by X-ray and microscopic methods.

2. Corundum is the stable phase above 450 ± 5°.

3. γ-Alumina is metastable throughout the range investigated.

4. Diaspore is stable below 450 ± 5°, and the lower limit for its stability seems to be around 280°.

5. Böhmite apparently is stable between 155 and 280°.

6. Gibbsite is unstable above 155°.

7. Bayerite is unstable above 155°, while the indications are that it is less stable than gibbsite below this temperature.

8. Diaspore has been prepared in the laboratory for the first time.

9. The value of seeding in phase rule studies has again been demonstrated.

ITHACA, N. Y. RECEIVED OCTOBER 15, 1942

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Studies in the Chromammines. II. Preparation of Luteo Salts[1,2]

BY CARL L. ROLLINSON[3,4] AND JOHN C. BAILAR, JR.

In the course of investigations concerning the chemistry of the chromammines, a convenient method for preparing salts of the tridiamine series was required. None of the available synthetic methods was found to be entirely satisfactory.

The reaction of an aqueous diamine with trichloro-tripyridine-chromium has been used for the synthesis of luteo[5] salts of the ethylene-

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[1] For the first paper in this series, see Balthis and Bailar, THIS JOURNAL, **58**, 1474 (1936).

[2] Presented at the 99th meeting of the American Chemical Society, Cincinnati, Ohio, April 9, 1940.

[3] Abstracted from a portion of a thesis submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in Chemistry at the University of Illinois, 1939.

[4] University Fellow in Chemistry. Present address, E. I. du Pont de Nemours & Co., Inc., Grasselli Chemicals Department, Cleveland, Ohio.

[5] In 1852 Fremy proposed a system of nomenclature for the cobalt ammonia compounds, utilizing the colors of the salts as the means of distinguishing between them. According to this system the salt now known as hexammine cobaltic chloride was given the name "luteo cobaltic chloride" (latin *luteus* = yellow). The meaning of the term was gradually extended to include the compounds of all trivalent metals coördinated with six ammonia or amine groups, regardless of color. Used in this way to describe a whole class of compounds, the term is still useful and convenient.

diamine,[6] propylenediamine,[7] *trans*-1,2-diaminocyclohexane and *trans*-1,2-diaminocyclopentane[8] series. The method is not convenient because anhydrous chromic chloride is not readily available and because long refluxing is required in the synthesis of [Cr py_3Cl_3].[9] Moreover, the formation of an insoluble red by-product in the reaction of the pyridine salt with the aqueous diamine seriously limits the yield of the desired product.

Another method for preparing triethylenediamine chromic salts is based on the reaction of ethylenediamine hydrate with dehydrated chrome alum.[10] While the starting materials are readily available, the yield is low because of formation of an insoluble red by-product and because the solution of the reaction mixture, from which the desired salts are obtained by metathetical reactions, cannot be evaporated below the minimum volume necessary to keep potassium salts in solution; considerable amounts of the luteo salts are thus not recoverable.

Tri-propylenediamine salts can be prepared by the action of aqueous propylenediamine on $K_3[Cr(SCN)_6]$.[7] This method, however, is not general; when ethylenediamine is used, the product is a mixture of *cis*- and *trans*-[Cr $en_2(SCN)_2$] SCN.[7,11,12]

It has also been shown that 1,2-diamines react with compounds of the type *cis*- or *trans*-[Cr en_2X_2]X (X = Cl, Br or SCN) to give tri-diamine salts.[13,14] These reactions are of little value in synthesis, however (except for the preparation of mixed salts such as [Cr en_2pn] Cl_3),[14,15] since the luteo salts themselves are the best starting materials for the preparation of the di-acido compounds, [Cr en_2X_2]X.[16]

Tri-diamino chromic salts are the final products of the reaction between diamines and chromous salts.[1] While the preparative method based on these reactions gives satisfactory yields, it is cumbersome and time-consuming.

The luteo salt, hexammine chromic chloride, is formed (along with chloro-pentammine chromic chloride) by the reaction of liquid ammonia with anhydrous chromic chloride. Investigation of the analogous reactions of anhydrous diamines with anhydrous chromic salts, therefore, appeared to be a logical approach in the development of an improved synthesis of tri-diamino chromic salts. Anhydrous chromic chloride may be used, but is not readily available. Anhydrous chromic sulfate, on the other hand, is easily prepared by heating the ordinary hydrated salt. It reacts readily with anhydrous ethylenediamine and propylenediamine (racemic and active) to give the luteo sulfates from which other salts are obtainable by metathesis. The yield of luteo sulfate is almost 100%; yields of salts prepared from the sulfate are limited only by solubilities.

Dehydrated chrome alum is also a convenient starting material. Modification of Pfeiffer's method[10] by the substitution of anhydrous for aqueous ethylenediamine is a distinct improvement, since the formation of the red by-product is avoided. Yields are somewhat limited, however, because of the presence of potassium salts, as previously discussed.

Attempts were made to prepare tri-trimethylenediamine salts by these reactions. No luteo salt was obtained, however, in the reaction of anhydrous trimethylenediamine with anhydrous chromic sulfate; the products were white amine salts and an uncrystallizable red sirup, probably containing basic salts. When $[Cr(NH_3)_5Cl]Cl_2$ was used instead of $Cr_2(SO_4)_3$ tarry products were obtained, the analyses of which approximated the calculated values for tri-trimethylenediamine chromic salts, but the results were inconclusive. Other investigators[7] have also reported unsuccessful attempts to prepare chromammines containing chelate rings of more than five members. Comparison of the products of these reactions with the well characterized crystalline luteo salts of 1,2-diamines indicates clearly the influence of ring size. The results may be explained by the assumption that instead of forming a six-membered chelate ring with one chromium atom, a molecule of trimethylenediamine links together two chromium atoms, with the formation of polymeric substances.

Since anhydrous chromic sulfate was found to be the most convenient starting material for the preparation of tri-diamino salts, attempts were made to ammonate it to the hexammine. It was found that no reaction occurs between chromic sulfate and boiling liquid ammonia or with

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[6] Pfeiffer, *Z. anorg. Chem.*, **24**, 286 (1900).

[7] Pfeiffer and Haimann, *Ber.*, **36**, 1063 (1903).

[8] Jaeger and Bijkerk, *Z. anorg. allgem. Chem.*, **233**, 128 (1937).

[9] The symbol "py" represents one molecule of pyridine.

[10] Pfeiffer, *Ber.*, **37**, 4277 (1904).

[11] The symbol "en" represents one molecule of ethylenediamine.

[12] Pfeiffer, *Ber.*, **37**, 4269 (1904).

[13] Pfeiffer, *ibid.*, **37**, 4265, 4270, 4278 (1904).

[14] Pfeiffer, *Z. anorg. Chem.*, **58**, 297 (1908).

[15] The symbol "pn" represents one molecule of propylenediamine.

[16] Rollinson and Bailar, THIS JOURNAL, to be pubished.

anhydrous gaseous ammonia at 80°. However, poor yields of hexammino chromic salts were obtained when chromic sulfate and chromic sulfate with ammonium chloride were sealed in tubes with liquid ammonia and kept at room temperature; in the experiment with ammonium chloride, it was thought that chromic chloride might be formed, since ammonium sulfate is insoluble in liquid ammonia.

The discouraging results of these reactions led to further investigation of the reaction of anhydrous ammonia with anhydrous chromic chloride. In this reaction the chloropentammine salt is supposedly an intermediate in the formation of the hexammine, which is produced in small amount. The chloropentammine does not ammonate further in boiling liquid ammonia, evidently because of its insolubility. Sealed with liquid ammonia at room temperature, it reacts very slowly, depositing crystals of the hexammine. The bromide, more soluble than the chloride, is ammonated somewhat more rapidly under these conditions, although the reaction is still too slow for practical purposes. A sample of the chloropentammine nitrate, however, sealed in a tube with liquid ammonia (in which the nitrate is quite soluble) was completely converted to the hexammine in about three hours at room temperature. A trace of sodamide, which is a base in liquid ammonia,[17] catalyzes this reaction; ammonation is catalyzed by the base, just as aquation is in many instances. It was then found that hexammino chromic nitrate can be prepared easily by ammonating chloropentammino chromic nitrate with boiling liquid ammonia containing a little sodamide, although conversion is not quite complete. The uncatalyzed reaction is extremely slow.

Experimental

Preparation of Materials.—Putnam and Kobe's method[18] for dehydrating ethylenediamine is very satisfactory and can be used for dehydrating propylenediamine and trimethylenediamine, which require only half the amounts of sodium hydroxide and sodium specified for ethylenediamine. The anhydrous bases are extremely hygroscopic.

Propylenediamine was resolved by Baumann's method.[19] The anhydrous l-propylenediamine used had the specific rotation $[\alpha]_D$ −7.8° (10-cm. tube, 2.05% aqueous solution); the completely resolved base has the specific rotation $[\alpha]_D$ −29.68°.[20]

Chrome alum was dehydrated by careful heating as described by Pfeiffer.[10] Anhydrous chromic sulfate was prepared by heating the hydrated salt in an oven at 110° for six days. After three days' heating the salt was ground to a powder. The final product was a fine green powder insoluble in water.

Chloropentammino chromic chloride was prepared by ammonation of anhydrous chromic chloride.[21] The nitrate and bromide were obtained by the action of an excess of nitric or hydrobromic acid on the chloride and purified by recrystallization from cold water. The order of solubility of the three salts in both water and liquid ammonia is nitrate > bromide > chloride.

Preparation of $[\mathrm{Cr\ en_3}]\mathrm{Cl_3 \cdot 3^1/_2H_2O}$ from Anhydrous Chromic Chloride.—Seven milliliters (0.09 mole) of anhydrous ethylenediamine was added to 3.17 g. (0.03 mole) of anhydrous chromic chloride. The violet salt swelled up and turned yellow, with evolution of heat. After the mixture was heated on the steam-bath for one hour, unchanged ethylenediamine was washed out with alcohol. The residue was dissolved in 6 ml. of water at 60° and filtered. Two milliliters of concentrated hydrochloric acid was added to the filtrate, which, after cooling on ice, deposited yellow crystals of the luteo salt. The product was recrystallized from 5 ml. of water at 60° and air-dried. The yield was 4 g. of $[\mathrm{Cr\ en_3}]\mathrm{Cl_3 \cdot 3^1/_2H_2O}$ (30%). *Anal.* Calcd. for $[\mathrm{Cr\ en_3}]\mathrm{Cl_3 \cdot 3^1/_2H_2O}$: Cr, 12.97. Found: Cr, 13.1.

Preparation of $[\mathrm{Cr\ en_3}]\mathrm{Cl_3 \cdot 3^1/_2H_2O}$ from Anhydrous Chrome Alum.—The following procedure was found to give good results. Twenty milliliters (0.3 mole) of anhydrous ethylenediamine is added to 28.3 g. (0.05 mole) of anhydrous chrome alum, and the mixture is heated[22] for several hours on the steam-bath. After the red-brown mass first produced has turned yellow, any excess ethylenediamine is washed out with alcohol. The solid is dissolved in 125 ml. of water (65°) and to the filtered solution is added 17 g. (0.3 mole) of ammonium chloride. The solution is cooled on ice and the crystals filtered off. The resulting luteo chloride is recrystallized from 25 ml. of water at 65°. The yield of crude $[\mathrm{Cr\ en_3}]\mathrm{Cl_3 \cdot 3^1/_2H_2O}$ is 23 g. (57%), of purified product 12 g. (30%). *Anal.* Calcd. for $[\mathrm{Cr\ en_3}]\mathrm{Cl_3 \cdot 3^1/_2H_2O}$: Cr, 12.97. Found: Cr, 13.1.

Preparation of $[\mathrm{Cr\ en_3}]\mathrm{Cl_3 \cdot 3^1/_2H_2O}$ from Anhydrous Chromic Sulfate.—The following procedure was found to be the best for preparing triethylenediamine chromic chloride. Forty-nine grams (0.125 mole) of $\mathrm{Cr_2(SO_4)_3}$ and 50 ml. (0.75 mole) of anhydrous ethylenediamine are heated[22] on the steam-bath until reaction starts; this is indicated when the sulfate begins to lose its bright green color and usually occurs within an hour after heating is started. From this point on, the flask must be shaken at intervals to keep the unchanged sulfate exposed to the amine. The flask is left on the steam-bath for at least twelve hours after the mass has turned brown. The product is ground to a powder and washed with alcohol. The yield of crude luteo sulfate is 89 g. (95%).

Thirty-two grams (0.04 mole) of luteo sulfate is dissolved in a mixture of 5 ml. of concentrated hydrochloric

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(17) Audrieth, *Z. physik. Chem.*, **A165**, 325 (1933).

(18) Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, 610 (1938).

(19) Baumann, *Ber.*, **28**, 1179 (1895).

(20) Tschugaeff and Sokoloff, *ibid.*, **42**, 55 (1909).

(21) Henderson and Fernelius, "Inorganic Preparations," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 130.

(22) Sometimes it is necessary to add a drop of water to start the reaction.

acid and 30 ml. of water at 60–65°. The solution is filtered rapidly and 27 ml. of concentrated hydrochloric acid dissolved in 42 ml. of alcohol is added to the filtrate which is cooled on ice and stirred. The chloride separates in pretty yellow crystals. The yield is 20 g. (60% based on luteo sulfate).

Twenty grams of this product, which is still contaminated with sulfate, recrystallized from 20 ml. of water at 65°, yields 12 g. of pure product, or 36% based on the luteo sulfate. *Anal.* Calcd. for $[\mathrm{Cr\ en_3}]\mathrm{Cl_3}\cdot 3^1/_2\mathrm{H_2O}$: Cr, 12.97; Cl, 26.5; ratio Cr/Cl, 0.489. Found: Cr, 13.08; Cl, 27.3; ratio Cr/Cl, 0.480.

Preparation of $[\mathrm{Cr\ en_3}]\mathrm{X_3}$ (X = Br, I or SCN) from $[\mathrm{Cr\ en_3}]\mathrm{Cl_3}\cdot 3^1/_2\mathrm{H_2O}$.—Thirty grams (0.075 mole) of luteo chloride is dissolved in 100 ml. of warm water and 0.45 mole (100% excess) of the required sodium or potassium salt added. The solution is stirred rapidly and cooled on ice. The luteo salt is filtered by suction and recrystallized from water at 65°, washed with alcohol and ether and air-dried. This procedure is based on that described by Pfeiffer.[23]

The yields, based on $[\mathrm{Cr\ en_3}]\mathrm{Cl_3}\cdot 3^1/_2\mathrm{H_2O}$ are: bromide 31 g. (76%), iodide 32 g. (68%), thiocyanate 23 g. (72%).

Anal. Calcd. for $[\mathrm{Cr\ en_3}]\mathrm{Br_3}\cdot 4\mathrm{H_2O}$: Cr, 9.56. Found: Cr, 9.54. Calcd. for $[\mathrm{Cr\ en_3}]\mathrm{I_3}\cdot\mathrm{H_2O}$: Cr, 8.27. Found: Cr, 8.17. Calcd. for $[\mathrm{Cr\ en_3}](\mathrm{SCN})_3\cdot\mathrm{H_2O}$: Cr, 12.24. Found: Cr, 12.12.

Preparation of $[\mathrm{Cr\ pn_3}]\mathrm{X_3}$, (X = Br, I, or SCN) from Anhydrous Chromic Sulfate.—From 39 g. (0.1 mole) of $\mathrm{Cr_2(SO_4)_3}$ and 55 ml. (0.6 mole) of anhydrous propylenediamine is obtained 74 g. of $[\mathrm{Cr\ pn_3}]_2(\mathrm{SO_4})_3$ (90%) by use of the same procedure as for the ethylenediamine salt. Other salts are prepared directly from the sulfate, since the chloride hydrolyzes readily to a basic salt.[24]

One one-hundredth mole of the sulfate is dissolved in 21 ml. of water at 65°. To the filtered solution is added 0.12 mole (100% excess) of the required ammonium salt in saturated solution. After cooling to 0°, the crystals are filtered by suction and recrystallized from water at 65°. The purified salt is washed with alcohol and ether and air-dried.

The yields, based on $\mathrm{Cr_2(SO_4)_3}$, are: bromide, 2 g. (20%), iodide, 9 g. (70%), thiocyanate, 5 g. (55%).

Anal. Calcd. for $[\mathrm{Cr\ pn_3}]\mathrm{Br_3}$: Cr, 10.10. Found: Cr, 10.15. Calcd. for $[\mathrm{Cr\ pn_3}](\mathrm{SCN})_3$: Cr, 11.60. Found: Cr, 11.80. Calcd. for $[\mathrm{Cr\ pn_3}]\mathrm{I_3}$: Cr, 7.95. Found: Cr, 8.10.

From a sample of anhydrous l-propylenediamine having the specific rotation $[\alpha]_\mathrm{D}$ −7.80° was obtained $[\mathrm{Cr\text{-}l\text{-}pn_3}]\mathrm{I_3}$, $[\alpha]_\mathrm{D}$ −14.0° (0.5% aqueous solution, 10-cm. tube).

Anal. Calcd. for $[\mathrm{Cr\ pn_3}]\mathrm{I_3}$: Cr, 7.95. Found: Cr, 8.0.

Reaction of Anhydrous Trimethylenediamine with Anhydrous Chromic Sulfate and with $[\mathrm{Cr(NH_3)_5Cl}]\mathrm{Cl_2}$.—Heating a mixture of equivalent amounts of anhydrous chromic sulfate and trimethylenediamine produced a purple-red mass from which no luteo chromic salts could be obtained.

Five grams (0.02 mole) of $[\mathrm{Cr(NH_3)_5Cl}]\mathrm{Cl_2}$ and 4.4 g. (0.06 mole) of anhydrous trimethylenediamine were heated for ten days on the steam-bath. The resulting brown mass was broken up, washed with alcohol and extracted with warm water to remove unchanged pentammino salt. Efforts to crystallize the material as the chloride, bromide or thiocyanate gave brown tars which solidified when rubbed with alcohol. It is supposed that these products were tri-(trimethylenediamine) chromic salts, but the analytical evidence was not conclusive.

Ammonation of Chromic Sulfate.—Anhydrous chromic sulfate was treated with anhydrous ammonia under a variety of conditions. No visible effect was produced within several hours by liquid ammonia at its boiling point (−33°) or within two days by gaseous ammonia at 80°. However, the green chromic sulfate sealed in a tube with excess liquid ammonia was converted to a brownish-red mass in three hours at +25°. The reaction product was dissolved in dilute nitric acid and the solution filtered from a small amount of residue. When concentrated nitric acid was added to the yellow filtrate, impure hexammine chromic nitrate precipitated. In another experiment, a mixture of anhydrous chromic sulfate and ammonium chloride was treated with liquid ammonia at 25°. The result was the same as before.

Ammonation of Chloropentammine Chromic Salts.—Samples of $[\mathrm{Cr(NH_3)_5Cl}]\mathrm{Cl_2}$, $[\mathrm{Cr(NH_3)_5Cl}]\mathrm{Br_2}$ and $[\mathrm{Cr(NH_3)_5Cl}](\mathrm{NO_3})_2$, each weighing a few grams, were sealed in small glass tubes with an excess of liquid ammonia and the tubes were allowed to come to room temperature. The depth of color of the solutions indicated that the solubility increases in the order $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NO_3^-}$; the chloride is almost completely insoluble. After four weeks, a few crystals of the yellow hexammine had formed in the tube containing the chloride. The bromide reacted more rapidly, but after a week conversion was far from complete. The nitrate, on the other hand, was completely converted to hexammine in three hours; the rate of this reaction was more than doubled by the addition of a trace of sodamide.

Boiling liquid ammonia at atmospheric pressure (−33°) reacts with the chloropentammine nitrate so slowly that no reaction could be observed when a sample of the salt was left dissolved in liquid ammonia for several hours. The addition of a trace of sodamide, however, brought about nearly complete conversion to the luteo salt in a few hours. Hexammine chromic nitrate can be prepared in excellent yields by this process. After the evaporation of the liquid ammonia, the product is dissolved in water, the solution filtered from the small residue of unchanged pentammino salt and the hexammine recovered as nitrate by the addition of concentrated nitric acid.

Anal. Calcd. for $[\mathrm{Cr(NH_3)_6}](\mathrm{NO_3})_3$: Cr, 15.26. Found: Cr, 15.1.

Quite different results were obtained with chloropentammine chromic chloride. No reaction was observed when a sample of this salt was left for several hours in boiling liquid ammonia containing a trace of sodamide. Nor could conversion be accelerated by passing gaseous ammonia at 80° over the solid pentammine chloride.

Summary

It has been shown that anhydrous 1,2-diamines react with anhydrous chromic chloride, chrome

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(23) Pfeiffer, *Z. anorg. Chem.*, **24**, 291 (1900).

(24) Balthis, Ph.D. Thesis, University of Illinois, **1934**, p. 39.

alum and chromic sulfate to give salts of the luteo type.

Improved methods for preparing luteo salts, based on the reactions of anhydrous diamines with anhydrous chromic salts, have been described.

Results of attempts to prepare tri-trimethylenediamine chromic salts were inconclusive.

It has been shown that ammonation under pressure of chloropentammino chromic salts depends on their solubility in liquid ammonia, the rate of reaction increasing in the order $Cl^- < Br^- < NO_3^-$, which is the order of increasing solubility in liquid ammonia. Hexammino chromic nitrate may be easily prepared by the sodamide-catalyzed ammonation of chloropentammino chromic nitrate at atmospheric pressure.

URBANA, ILL. RECEIVED OCTOBER 16, 1942

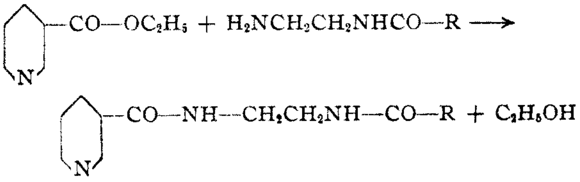
[CONTRIBUTION FROM THE FOOD AND DRUG LABORATORY, FLORIDA DEPARTMENT OF AGRICULTURE]

Derivatives of Pyridine Acids. I. N-(2-Acylaminoethyl)-nicotinamides

BY ERNEST M. HODNETT AND VINCENT E. STEWART

Compounds containing the nicotinic acid group exhibit a variety of physiological properties. Those in which the nicotinic acid is contained in an amide linkage are of most recent interest. In order to further this study it was considered desirable to combine this group with the ethylenic linkage, which is also characteristic of some compounds possessing medicinal properties.

Monoacylethylenediamines were prepared by the method of Hill and Aspinall.[1,2] These were treated with ethyl nicotinate[3] by heating in equimolecular proportions for several hours at about 100°. The reaction proceeded as follows



Upon cooling to room temperature the reaction mixture crystallized, and the N-(2-acylaminoethyl)-nicotinamide was purified by recrystallization. The products were characterized by analysis and by the preparation of hydrochlorides and picrates.

Acetylethylenediamine, propionylethylenediamine, butyrylethylenediamine, valerylethylenediamine and caproylethylenediamine were treated with ethyl nicotinate to yield the corresponding substituted nicotinamide.

Hydrolysis of N-(2-acetylaminoethyl)-nicotinamide by refluxing with dilute hydrochloric acid or phosphoric acid yielded the expected products: nicotinic acid (hydrochloride), ethylenediamine (hydrochloride), and acetic acid. Nicotinic acid was identified by mixed melting point determination with an authentic sample, ethylenediamine by the analysis of chloride in the hydrochloride, and acetic acid by determination of the Duclaux constant.

Experimental

N-(2-Acetylaminoethyl)-nicotinamide.—One-half mole (75.5 g.) of ethyl nicotinate and one-half mole (51.0 g.) of acetylethylenediamine were heated at 100° for fifteen hours. The reaction mixture began to crystallize after four hours of heating. The crude product was recrystallized from a mixture of alcohol (1 vol.) and benzene (3 vols.). The weight of dry product after one recrystallization was 60.8 g. (58.7%). The sample taken for analysis of nitrogen by the Kjeldahl method was recrystallized four times in the above manner; m. p. 170–171° (cor.).

Anal. Calcd. for $C_{10}H_{13}N_3O_2$: N, 20.3. Found: N, 20.3.

The higher homologs were prepared and purified in a similar manner. N-(2-Acylaminoethyl)-nicotinamides which have been investigated are very soluble in water, alcohol and chloroform. The lower members are moderately soluble in hot benzene and insoluble in carbon tetrachloride and ether, while the higher members are very soluble in hot benzene, soluble in hot carbon tetrachloride, and soluble in ether. The hydrochlorides are soluble in water and are recrystallizable from a mixture of alcohol and ether. The picrates are also soluble in water and are recrystallizable from alcohol.

The compounds were digested with difficulty in preparation for analysis of nitrogen by the Kjeldahl method. The analysis was more nearly in accordance with the theoretical content when both copper sulfate and selenium were used as catalysts and the digestion was started over a low flame and gradually increased during about thirty hours.

Pharmacology

The pharmacology of the compounds which have been synthesized was studied by Dr. C. C.

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(1) Hill and Aspinall, THIS JOURNAL, **61**, 822 (1939).

(2) Aspinall, *ibid.*, **63**, 852 (1941).

(3) McElvain and Adams, *ibid.*, **45**, 2738 (1923).