In this case, the results obtained by calculation from the percentages of nitrogen and sulphur, are almost identical with those obtained by direct determinations. But the greater ease and certainty of the direct method, and the very considerable errors which are possible when calculations are instituted upon results differing but very slightly from the true ones, must strongly recommend, it appears to us, the direct as compared with the indirect method.

If the mustard is adulterated with starch or flour, the foregoing scheme of analysis may be used as well in the case of pure mustard. After the extraction of the oil with ether, and the sulphocyanide of sinapine and myronate of potash with alcohol, the residue may be treated either with malt extract or with acids under pressure to convert the starch into glucose. The glucose may be estimated as usual.

Fearing that starch was not entirely insoluble in dilute alcohol, and not being able to learn anything on the subject from books, an experiment was made of boiling starch for some time in a mixture of half alcohol and half water. The boiling liquid was filtered hot, and to the filtrate a few drops of iodine solution added. No blue coloration taking place, the starch may be considered insoluble in dilute alcohol, and hence could not interfere in the determination of the sulphocyanide of sinapine and myronate of potash.

XXXIV.—UPON THE COMPOUNDS OF THE AROMATIC BASES WITH METALLIC SALTS, WITH A NOTE UPON THIOCARBANILIDE.

By ALBERT R. LEEDS.

Introduction.

The author was led to a study of these compounds by the following considerations :—

I. The energy, in many cases attended by the evolution of much heat, with which a number of them are formed.

II. The hope that a study of the structural formulæ of compounds of so considerable a degree of complexity, and containing both metallic and non-metallic basic radicals in combination with acid radicals, might be attended with theoretic interest.

III. The expectation, which, indeed, first suggested the inquiry, that by removal or replacement of the metallic element in these compounds by reactions, induced by organic compounds of sulphur and related substances, these metallo-aromatic bodies would serve as material in the institution of an interesting line of research. This expectation was in part verified, such derivatives being obtained either by laboratory operations, conducted as usual, or with the aid of sun-light, but it was then found that they had already been prepared by simpler and more direct methods. These remarks apply more especially to thiocarbanilide and related compounds.

But it was found that the great majority of these compounds were quite unstable, undergoing decomposition merely by treatment with water. Consequently, the attempts to form them by double decomposition of aqueous solutions of their constituent salts were mainly unsuccessful. Moreover, the double salt of the aromatic base, containing the same acid radical in combination with both base and metal, could not be formed. This result is in opposition to that obtained by Schiff, not only in the case of antimonious chloride, but also in regard to other compounds. Finally, if the combinations are to be regarded as either amines or ammoniums, in which a portion of the hydrogen is replaced by a metal, and the radical thus formed enters into combination with either the acid itself or the acid radical, then it might be anticipated that such a compound would again unite with platinic chloride to form a double salt. Numerous attempts were made to form such double salts, but they were unsuccessful, the metallic salt dropping out, and a double chloride of platinum and the aromatic base alone remaining.

In formulating them, therefore, as ammoniums, which is the simplest mode of explaining their composition, these points of weakness in the experimental data must be kept in mind. And whilst the following compounds might receive a nomenclature in accordance with the theory of their being metallo-ammoniums, the antimony compound being the chloride of triphenylstibonium, the salt of mercury being the chloride of diphenylmercurammonium, and so on, yet I have seldom used these terms, not only because of their cumbrous character, but also because they necessarily assume what as yet is not very satisfactorily proven.

Authorities consulted.

H. Schiff: Upon the Anilo-metallic Compounds and upon the Formation of Fuchsine. C. R. 56, 268.

H. Schiff: Researches upon the Mercuraniles, C. R., 56, 491.

" " Researches upon the Trimetalaniles, C. R., 56, 1095.

C. Foster: Upon Mercuridphenylammonchlorur, $NC_6H_5.Hg.HCl$. *Ber. der Deutsch. Chem. Gesell.*, 7, 294.

O. Klein: Upon the Combinations of Organic Bases with Mercuric Chloride. *Ber. der Deutsch. Chem. Gesell.*, 11, 743 and 1741.

LIPPMANN and VORTMANN: Upon a Combination of Cobaltous Chloride with Aniline. *Ber. der Deutsch. Chem. Gesell.*, **II**, 1069.

Watts' Dictionary of Chemistry.

Beilstein's Lehrbuch der Organischen Chemie, pp. 875 and 936.

Compounds with Aniline.

I. ALUMINA SALTS.

Aluminic chloride.—Three molecules of aniline were heated with one of aluminum chloride. The resulting compound was washed with alcohol, water and ammonium chloride, in none of which it appeared to dissolve. After washing out all the excess of aniline with alcohol, a white crystalline powder remained.

The operation was repeated, alcohol only being used to dissolve the resultant compound. The crystals which separated out of the first portions of the alcohol, proved to be chloride of aniline. The white powder which remained after repeated treatment with boiling alcohol, was alumina. In other words, no compound of aniline with aluminic chloride is formed when the former is heated with Al_2Cl_6, $6H_2O$. The latter is decomposed into alumina and hydrochloric acid, and merely a hydrochlorate of aniline is formed.

Aluminic sulphate.—On mixing the two bodies, only a slight elevation of temperature ensued, and the heat was afterwards raised to the boiling point of aniline. The excess of aniline was washed out by repeated decantation with boiling alcohol, in which it is not very soluble, and a portion of the compound crystallized from the same solvent. It crystallized, apparently, in small white needles. On heating, these crystals blackened, and burnt with a small flame. Their analysis gave only 4.4 per cent. of alumina. The compound $3C_6H_7N.Al_2(SO_4)_3$, requires 8.84 per cent. of alumina. They were not a compound with aniline, but some of the undecomposed sulphate together with aniline which had not been perfectly removed by repeated washing.

Aluminic hydrate.—Neither this nor any other salt of alumina entered into combination.

II. ANTIMONY.

Antimonious chloride, $3C_6H_9N.SbCl_3$.—First formed by adding 3 molecules of aniline to one of antimonious chloride and heating. The resulting compound had a pinkish color, probably due to exposure to the air. It lost this color after washing with alcohol, and became perfectly white. It was decomposed by water.

Schiff prepared this substance as above, and also by adding aniline to a solution of antimonious chloride in benzine. This yielded a white crystalline mass, which was soluble in aniline only, and crystallized out of the latter in slender needles. According to Schiff, it is converted into a double salt by hydrochloric acid, melts at 80°, solidifies again in long needles, and is partially decomposed by distillation (Watt's Dictionary, **4**, 474).

These statements were not verified. On the addition of hydrochloric acid the compound was decomposed, hydrochlorate of aniline crystallizing out of the solution. It does not melt at 80°, nor even at 240°, being in part decomposed and partially subliming. This was true both when heated in the air, and when the attempt was made to distil it in vacuo.

When the same compound was made by mixing antimonious chloride with aniline, the temperature rose from 23°.5 to 82°.5. It was washed repeatedly with alcohol, in which it is but slightly soluble, and a portion recrystallized from the same. It formed minute needle-shaped crystals. It was decomposed by water, the solution giving the reaction for antimony and aniline.

Antimonic chloride, $5C_6H_7N.SbCl_5$.—Formed in like manner as the preceding compound, which it closely resembles in appearance and properties. The temperature rose from 22°.5 to 85°.

Antimonious iodide, $3C_6H_7N.SbI_3$.—"To obtain the combination of antimonious iodide with aniline, it is necessary to raise the temperature to 100° or 120°. If an excess of aniline is used, the compound is formed in little yellow needles, colored undoubtedly by a small quantity of iodine. By distillation a large portion is decomposed" (Schiff).

I did not repeat the experiment.

Antimonious sulphide.—Does not enter into combination.

III. ARSENIC.

Arsenious chloride, $3C_6H_7N.AsCl_3$.—On the addition of 3 molecules of aniline to one of arsenious chloride, an energetic combination ensued, the temperature being considerably raised, and the mixture solidifying afterwards to a whitish crystalline mass. This was purified by recrystallizing three times from alcohol. The final product was in small white crystals, not well defined and becoming red by exposure to the air.

According to Schiff (*loc. cit.*), this compound melts at about 90°, distils without decomposition between 205° and 210°, and is somewhat soluble in water, with separation of arsenious acid. We sublimed it in vacuo, at circa 205°, at which temperature it sublimes without previous melting and with partial decomposition. The product lost the red tint of the original substance, and was in the form of minute white plates, polarizing finely. It was decomposed by hydrochloric acid, and after slow evaporation of the hydrochloric acid solution, only aniline hydrochlorate remained, the $AsCl_3$ having volatilized.

Arsenious iodide, $3C_6H_7N.AsI_3$.—"It forms at an elevated temperature, and is decomposed neither by cold water nor by dilute hydrochloric acid. It is slightly soluble in benzine and in cold alcohol. Boiling alcohol decomposes it in a curious manner; brown flocks of monoiodide of arsenic are obtained, and the alcohol on evaporation leaves long needles of hydriodide of iodoaniline" (Schiff).

$$3C_6H_7N.AsI_3 = AsI + C_6H_6IN.HI + 2C_6H_7N.$$

The experiments were not repeated.

Arsenious sulphide.—Does not enter into combination.

IV. BARIUM.

No combination ensued when aniline was subjected to the action of barium acetate, chloride, iodide, nitrate and sulphide.

On heating aniline with barium chloride or iodide, dissolving in boiling ammonium chloride, and crystallizing, small white needles were formed. On the addition of water, these went into solution very readily. After washing with alcohol, they were found to consist only of unchanged barium chloride or iodide. When the mass obtained by heating aniline with the barium salt was treated with alcohol, no compound could be crystallized out.

V. BISMUTH.

$3C_6H_7N.BiCl_3$.—According to Schiff (*loc. cit.*), this is a fusible, indistinctly crystalline mass, which is very slowly decomposed by water, and turns violet when heated. The experiment was not repeated. I found that the nitrate formed no compound.

VI. CADMIUM.

Cadmium chloride, $2C_6H_7N.CdCl_2$.—This and the corresponding compounds of cadmium bromide and iodide, were obtained by heating with excess of aniline. On boiling all went into solution, but after cooling the entire mass crystallized in a solid lump. The excess of aniline was washed out with alcohol, in which these cadmium compounds are insoluble. Neither could they be crystallized from chloroform, ether, or water. Ammonia exercised a solvent action, but appeared at the same time to effect some decomposition. The three compounds were boiled with calcium chloride, in which they were readily soluble, and from which they crystallized out in fine white needles. The $2C_6H_7N.CdCl_2$ was purified from $CaCl_2$ by redissolving in water, from which it crystallized in very minute, flexible needles, of a white color, with silky luster. These needles readily compacted themselves into soft, tufted masses.

As crystallized from ammonium chloride, all the compounds formed by aniline with cadmium or other salts were not pure. It was found to be the best method, in almost all instances, to heat the salt directly with the aniline, and, after getting rid of the excess of the latter, to crystallize repeatedly out of alcohol. When the cadmium chloride was so made, the temperature rose from 18° to 42°.

Cadmium bromide, $2C_6H_7N.CdBr_2$, as crystallized from calcium chloride, formed longer needles, which aggregated in little tufts and had a satin luster.

Cadmium iodide, $2C_6H_7N.CdI_2$.—This compound, when recrystallized from boiling ammonium chloride, formed like the two former when crystallized from the same solvent, long thick white needles. The needles were flat, and of a beautiful pearly luster. On exposure to light and air their color turned to a faint pink.

Cadmium nitrate, $2C_6H_7N.Cd(NO_3)_2$.—It was obtained by boiling cadmium nitrate with excess of aniline, and washing out the latter with alcohol. It crystallizes in white needles, aggregating into lamellar masses, with a silky luster.

VII. CALCIUM.

Calcium chloride, $2C_6H_7N.CaCl_2$.—On mixing aniline with calcium chloride, the temperature rose from 18° to 20°. The mixture was then raised to the boiling point of the aniline, when, on cooling, a hard crystalline mass was formed. This was drained from the excess of aniline, pulverized, and dried between filter paper. On account of the extreme solubility of the compound in alcohol, it was washed only once in this solvent, and then dissolved and crystallized. It formed long, stout prisms, perfectly colorless, and of a glacial appearance.

$2C_6H_7N.CaI_2$.—The temperature of the mixture rose from 20°.5 to 24°. It behaved exactly like the corresponding chloride, forming crystals similar to those above described.

Experiments made with a view of crystallizing out the compounds from boiling ammonium chloride, were not satisfactory, owing to their great solubility both in water and alcohol.

VIII. CHROMIUM.

Neither chromic chloride or sulphate entered into combination.

IX. COPPER.

When cupric acetate is added to aniline, the mixture immediately becomes black, and solidifies to a very hard mass. In order to insure complete union this mass was broken up and triturated in a mortar with aniline. After washing several times with alcohol and boiling it with the same, there was left a black, uncrystallizable mass. When dissolved in hydrochloric acid this substance gave no reaction for aniline.

Cuprous chloride and cupric nitrate.—Similar black substances were produced, and no certain evidence was obtained that definite compounds with these salts were formed, or if formed, were stable in contact with air or solvents. The same results were true of cupric sulphate.

X. COBALT.

Cobaltous chloride, $2C_6H_7N.CoCl_2$.—When the cobaltous chloride and aniline were mixed together, the temperature of the mixture rose from 18°.5 to 104°.5. The resulting compound was washed several times with alcohol. Finally one portion was recrystallized from absolute, the other from common alcohol. Both formed very beautiful red crystals, the former in rhomboidal plates, the latter in prismatic needles. When exposed to the air, these crystals assume a cobalt blue color.

The constitution of these bodies has already been investigated by Lippmann and Vortmann, who formed the first substance as a pale red precipitate by the addition of an alcoholic solution of cobaltous chloride to aniline. They found its composition to be $2C_6H_7N.CoCl_2 + 2C_2H_6O$. The blue compound is derived from the former, by spontaneous decomposition in the atmosphere, forming $2C_6H_7N.CoCl_2$.

We found, as had already been shown by the authors abovementioned, that these compounds are decomposed into their constituents on solution in water. Also that on treatment with an alcoholic solution of platinic chloride, a double salt with aniline, not containing in combination the cobaltous chloride. is formed.

Cobaltous nitrate and sulphate.—In aqueous or alcoholic solutions, or when heated directly with aniline, these salts did not combine.

XI. IRON.

Ferric chloride.—On adding ferric chloride to aniline, so energetic a reaction ensued that the temperature of the mixture rose to 80°. A black mass was formed, incompletely soluble in alcohol and water, and which could neither be sublimed nor crystallized from any solvent which was employed.

Ferrous chloride, $2C_6H_7N.FeCl_2$.—On adding aniline to ferrous chloride the temperature is raised from 21° to 23°. It solidifies to a hard yellowish mass. After removing the excess of aniline by washing with alcohol, and dissolving in alcohol, the compound crystallizes in yellowish needles.

Ferrous sulphate.—It does not enter into combination.

XII. LEAD.

None of the salts of lead form compounds with aniline.

XIII. MAGNESIA.

The same is true of the magnesia salts.

XIV. MANGANESE.

Manganous chloride, $2C_6H_7N.MnCl_2$.—An alcoholic solution of two molecules of aniline was added to one molecule of manganous chloride likewise dissolved in alcohol. A cloudiness formed immediately, and the compound slowly crystallized out as beautiful white rhombic plates, with a pearly luster.

When the compound with manganous chloride was formed by direct addition of aniline, the temperature rose from 18° to 24°

Manganous bromide, $2C_6H_7N.MnBr_2$.—By direct mixing of the constituents, a rise of temperature from 21° to 40° resulted. It separated from alcohol in small colorless crystals.

Manganous iodide, $2C_6H_7N.MnI_2$.—The temperature rose from 21° to 39° The small, colorless crystals obtained from the alcoholic solution were similar to the bromine compound.

Manganous sulphate.—It did not enter into combination.

XV. MERCURY.

Mercuric chloride, $2C_6H_7N.HgCl_2$.—"It is precipitated on adding mercuric chloride to an excess of alcoholic aniline. It is a nacreous precipitate, which must be collected on a filter and washed with a small quantity of alcohol. It gives off a small quantity of aniline even at 60°, and turns yellowish (Gerhardt, Traité, 3, 86). According to Schiff, it decomposes at 100°, yielding aniline-red, and a similar red product is obtained by heating aniline with mercurous chloride to 150°. (Probably the aniline used contained toluidine.)" Watts' Dict., 4, 475.

I obtained the salt by heating the aniline directly with mercuric chloride and crystallizing out of ammonium chloride. The crystals were several millimeters in length, and of a yellowish-white color. They were not pure, and the compound is best obtained by heating aniline directly with mercuric chloride. It crystallized from alcohol in small white needles. The combination with mercuric chloride caused an elevation of temperature from 24° to 106°.

$NC_6H_5.Hg.HCl$.—According to Foster (*Ber. der Deutsch. Chem. Gesell.*, 7, 294), this compound is produced together with $2C_6H_7N.HgCl_2$ when the boiling solutions of aniline and mercuric chloride are mixed together. The $2C_6H_7N.HgCl_2$ remains in solution, whilst the new compound, a "phenylated white precipitate," settles as a yellow precipitate, and by repeated exhaustion with boiling alcohol may be obtained pure. The above formulæ was in accordance with the analysis :—

	Theory.	*Found.*
C	21.98	21.60
H	1.83	2.00
N	4.28	4.52
Cl	10.84	11.15
Hg	61.07	60.96-61.47.

Mercurous chloride.—It could not be made to enter into combination.

Mercuric iodide, $2C_6H_7N.HgI_2$.—After dissolving mercuric iodide in boiling aniline, the solid mass which formed on cooling was dissolved in boiling ammonium chloride, filtered and crystallized. Prismatic needles were formed of considerable size, which decomposed on attempting to further purify them by recrystallization from water.

According to Schiff, this compound forms little yellowish leaves, which can be obtained from the nitrate by double decomposition.

This statement of Schiff could not be verified. Neither could a compound be crystallized out from a solution of the mass, formed by heating aniline with mercuric iodide, in alcohol. No evidence of the existence of a compound of these two bodies could be obtained.

Klein states that he formed the compound $2C_6H_7N.HgI_2$ with a melting point of 60°.

Mercuric bromide, $2C_6H_7N.HgBr_2$.—No attempt to make it. Formed, according to Klein, in long crystals when crystallized out of alcohol. M. pt., 110°–112°. Decomposed by boiling water.

Mercuric nitrate, $2C_6H_7N.Hg(NO_3)_2$.—According to Schiff, this is obtained as a white precipitate, when aniline is added to a solution of mercuric nitrate. The powder becomes crystalline if it is digested, while still moist, with cold dilute nitric acid. Small brilliant leaves are obtained, if a solution of the slightly acidulated nitrate is used, or if the neutral mercuric solution is added drop by drop to an acidulated solution of nitrate of aniline. In every case the same compound is formed and not the double salt. The salt is unalterable in the air, and slightly soluble in dilute nitric acid.

"When heated with water, the salt yields aniline nitrate and changes to a dense white crystalline powder, $C_6H_5.NH.HgNO_3$."

"This last salt, diffused during several days with a large quantity of boiling water, gives up more aniline nitrate, and forms $(C_6H_5N)_2$-$Hg_3(NO_3)_2 + 2H_2O$. When heated with water for eight more days, this last compound suffers no further alteration."

Mercurous nitrate.—"Mercurous nitrate likewise combines with aniline to form $2C_6H_7N.Hg_2(NO_3)_2$, a white crystalline powder, very readily decomposed by a slight elevation of temperature, with reduction of the mercury."

The above statements of Schiff, with regard to the compounds of mercuric and mercurous nitrate, could not be verified, and no proof was obtained of the existence of any of the bodies above spoken of.

When mixed with aniline, the mercurous nitrate caused an elevation of temperature from 21°.5 to 79°.5, and the mass increased greatly in volume, forming a black crystalline substance. After removing the excess of aniline it was dissolved in alcohol, from which it did not crystallize satisfactorily.

This fact, together with the circumstance that the crystals in aqueous solution gave no reaction for aniline, shows that no compound was formed.

Mercuric cyanide, $2C_6H_7N.HgCy_2$.—On adding powdered mercuric cyanide to aniline, the rise of temperature was only from 17° to 21°, and in order to insure complete combination, the mixture was heated to the boiling point of the aniline. The latter being in excess, it dissolved the resulting compound at the same time that it entered into combination with the cyanide, and on cooling and standing the $2C_6H_7N.HgCy_2$ was deposited as stout prisms, six-sided, and of a vitreous luster. These crystals were freed from adhering aniline by washing with alcohol.

According to Schiff, $2C_6H_7N.HgCy_2$ separates in long, magnificent needles on mixing aniline with a hot aqueous solution of mercuric cyanide. It melts very readily, and is resolved into aniline and cyanide of mercury at 80°. It is attacked neither by alkalies nor by biniodide of potassium.

XVI. NICKEL.

Nickel chloride, $2C_6H_7N.NiCl_2$.—It united directly with aniline, the temperature rising from 20° to 40°. The product solidified to a dark green mass, which crystallized out of alcohol in clusters of green needles. It altered in color on keeping.

According to Lippmann and Vortmann, who prepared this compound somewhat differently, the body obtained from alcohol contains $2C_6H_7N.NiCl_2.2C_6H_6O$, and gives off alcohol at 100°, becoming yellowish-green, and forming $2C_6H_7N.NiCl_2$.

Nickel sulphate.—Does not enter into combination.

XVII. PALLADIUM.

Palladium chloride formed a compound, but the amount of the salt at my disposal was too small to admit of study.

XVIII. PLATINIC CHLORIDE AND PLATINOUS CHLORIDE.

The former does not combine. The compounds of the latter will be found described in Beilstein's Handb. der Organ. Chemie, p. 875.

XIX. POTASSIUM.

No combination ensued between aniline and potassium iodide, or with the other salts of potassium experimented upon.

XX. STRONTIUM.

Its salts do not combine with aniline.

XXI. TIN.

Stannous chloride, $2C_6H_7N.SnCl_2$.—"It is obtained by mixing the same number of equivalents of stannous chloride and aniline. A slight evolution of heat occurs, and at the end of some hours a crystalline mass is obtained which is slightly soluble in cold water and in alcohol, but which is decomposed by these liquids on warming" (Schiff).

On mixing aniline with stannous chloride the temperature rose from 22° to 35°. The compound crystallized out of alcohol in small white needles (Leeds).

Stannic chloride, $4C_6H_7N.SnCl_4$.—"It has been obtained by the union of 2 equivalents of aniline to 1 eq. of stannic chloride. An intense heat is produced at the moment of mixture, and it is necessary, to avoid explosions, to place the vase in a cooling mixture. Under these conditions, a perfectly white crystalline mass is obtained" (Schiff).

"Or if one adds the aniline drop by drop to a solution of stannic chloride in benzine, a white crystalline powder is seen to deposit at once, which is the $4C_6H_7N.SnCl_4$, insoluble in benzine. It is decomposed by water, stannic hydrate being precipitated" (Schiff).

When stannic chloride was added, the temperature rose from 21° to 60°. Its crystallization from alcohol yielded small white needles, turning bluish-gray after a long interval (Leeds).

Stannous iodide, $2C_6H_7N.SnI_2$.—The temperature rose from 21° to 40°, and the compound crystallized out of alcohol in grayish-white needles.

XXII. TITANIUM.

Titanium chloride, $4C_6H_7N.TiCl_4$.—The flask which contained the titanium chloride was broken, and the vapor allowed to flow down in contact with the aniline. It was energetically absorbed, forming a hard mass of a reddish color. This was dissolved in alcohol, the compound separating out in white, feathery crystals.

XXIII. URANIUM.

Uranium acetate.—Formed no compound.

Uranyl chloride, $2C_6H_7N.UO_2Cl_2$.—The chloride in alcohol solution was added to the alcoholic solution of aniline, and allowed to stand. The compound was slowly precipitated out as small yellow needles. Owing to their solubility in alcohol they were washed with ether, and afterwards recrystallized from alcohol. No elevation of temperature was noted on mixing the alcoholic solutions.

Uranium nitrate entered into combination under the same circumstances as the chloride, but the precipitate formed immediately on mixing the alcoholic solutions, as a heavy yellow crystalline compound.

XXIV. ZINC.

Zinc chloride, $2C_6H_7N.ZnCl_2$.—"Crystallizes in oblique, rhomboidal prisms, anhydrous, soluble in water and in alcohol, especially in the cold. By prolonged boiling of these solutions the salt is decomposed into aniline and zinc chloride. It combines with platinic chloride, forming granular crystals" (Schiff).

Zinc iodide, $2C_6H_7N.ZnI_2$.—On adding the zinc salt to an excess of aniline, the temperature rose from 17°.5 to 63°, and the substances united to form a white mass, which became very hard and compact. The excess of aniline was removed by washing with a small amount of alcohol. The residue was dissolved by digesting with alcohol under a return cooler, and after two recrystallizations became quite pure. It formed unusually brilliant prismatic needles of about a centimeter in length, with a pearly luster, and aggregating into radiate clusters.

Zinc bromide, $2C_6H_7N.ZnBr_2$.—It was prepared in like manner, the temperature of the mixture rising from 16° to 62°. The crystals were similar to those of the foregoing compound, but not so long or brilliant.

Zinc sulphate.—"It is more soluble than the preceding salts, and can be used with advantage to prepare them by the method of double decomposition" (Schiff).

I did not succeed in forming a compound with zinc sulphate.

Compounds with Paratoluidine.

I. CADMIUM.

Cadmium nitrate, $2p\text{-}C_7H_9N.Cd(NO_3)_2$.—The first method employed in making this compound was by the addition of an aqueous solution of paratoluidine nitrate to an aqueous solution of cadmium nitrate, both salts being in molecular proportions. But the toluidine nitrate crystallized out separately.

The second method was by heating the cadmium nitrate directly with paratoluidine. A solid white mass was formed, which yielded, when recrystallized from benzine or alcohol, white needles compacted together like leaves.

Cadmium bromide, $2p\text{-}C_7H_9N.CdBr_2$.—It was prepared by mixing together the alcoholic solutions of the two bodies in molecular proportions, and precipitated as a dense white crystalline mass.

Cadmium iodide, $2p\text{-}C_7H_9N.CdI_2$.—From the alcoholic solutions it was precipitated in white prismatic needles, which were washed with alcohol. It was also formed by heating the cadmium iodide directly with fused paratoluidine, and recrystallization from alcohol. The temperature of the fused mass rose from 67° to 90°.

II. COPPER.

On the addition of paratoluidine nitrate in aqueous solution to an aqueous solution of cupric nitrate, a dark green precipitate was obtained, which speedily blackened. On standing, crystals of impure toluidine nitrate formed on the sides of the vessel, and a blackish mass containing copper and some organic matter was left behind. But no definite compound could be isolated.

A similar change took place in the compound formed on the addition of cupric chloride to paratoluidine hydrochlorate, an uncrystalline blackish mass remaining.

III. COBALT.

On mixing the aqueous solutions of the nitrates, no compound was formed, the constituents crystallizing out separately, with the formation of a small amount of a blackish mass, due to partial decomposition.

The chlorides, likewise, did not enter into combination when their aqueous solutions were mixed together.

Lippmann and Vortmann have already explained the reaction* when an alcoholic solution of cobaltous chloride is added to paratoluidine.

IV. CHROMIUM.

Chromium sulphate.—After mixing the aqueous solutions of the two salts, they were allowed to evaporate spontaneously, when the constituents crystallized out separately.

Chromic chlorides.—A solution of chromic acid was reduced by alcohol and hydrochloric acid to Cr_2Cl_6, and added to an alcoholic solution of paratoluidine. The solutions solidified to a brown mass, from which, on treatment with water, the toluidine chloride crystallized out, leaving the chromium sesquichloride behind as a green powder.

V. GOLD.

One mol. of auric chloride dissolved in alcohol, was added to three molecules of toluidine dissolved in the same solvent. The liquid became dark purple and after a time deposited a sediment due to the reduction of the gold salt.

VI. MERCURY.

Mercurous nitrate, $2p\text{-}C_7H_9N.Hg_2(NO_3)_2$.—It was formed on adding an aqueous solution of toluidine nitrate to an aqueous solution

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* *Ber. der Deutsch. Chem. Gesell.*, **12**, 81.

of mercurous nitrate, acidified with nitric acid. The salt separated out slowly in small opaque white needles. It was purified by washing with cold water; in hot water, acidified with nitric acid, it dissolved readily.

Mercuric nitrate.—The corresponding mercuric salt could not be obtained in a crystalline condition. The precipitate obtained on evaporating the aqueous solutions of toluidine nitrate and mercuric nitrate to a small bulk, was easily soluble in water, but would not crystallize from the solution.

Mercuric chloride, $2p\text{-}C_7H_9N.HgCl_2$.—It was obtained by adding 2 mols. of toluidine dissolved in alcohol to 1 mol. of mercuric chloride, likewise in alcoholic solution, and dissolving the precipitate in boiling ammonium chloride. It crystallized out in white needles an inch in length, which decomposed on treatment with water. For this reason the toluidine and mercuric chloride were heated together until combination ensued, the resulting compound dissolved in alcohol, and recrystallized from the same solvent. The crystals in this case were white also, but not of such great length as those obtained from the ammonium chloride solution.

According to Klein, it crystallizes out of ether in magnificent thick needles, and decomposes at 70°, giving off paratoluidine.

Mercuric cyanide, $2p\text{-}C_7H_9N.HgCy_2$.—Formed like the corresponding aniline compound, and crystallizing similarly. The crystals are much larger and have an adamantine luster.

VII. MANGANESE.

$2p\text{-}C_7H_9N.MnCl_2$.—This was prepared both by adding the alcoholic solutions of the two components, and by adding the manganese chloride to fused paratoluidine. It could not be obtained in pure white crystals, but only as a faint red crystalline powder.

VIII. SILVER.

One mol. of argentic nitrate dissolved in water was added to an aqueous solution of toluidine nitrate. No combination occurred, the toluidine nitrate crystallizing out in long white needles.

IX. URANIUM.

$2p\text{-}C_7H_9N.UO_2Cl_2$.—The attempt to prepare the salt by mixing the aqueous solution of uranyl chloride with an aqueous solution of toluidine hydrochlorate was unsuccessful: the yellow solution deposited a pink powder, while the toluidine hydrochlorate crystallized out.

No better result was obtained with the alcoholic solutions of uranyl chloride and of toluidine. The uranium salt separated out on standing as a yellow powder, and the toluidine alone crystallized from the alcohol.

In a third trial the alcoholic solutions of the two bodies in molecular proportions were mixed together, the alcohol evaporated off, and the residue dissolved in aniline. After long standing the compound crystallized out in long, thick, greenish-yellow prisms, apparently orthorhombic and doubly terminated. They were drained from the excess of aniline by pressing with filter paper, and washed with a little alcohol.

X. ZINC.

Zinc bromide, $2p\text{-}C_7H_9N.ZnBr_2$.—Formed by adding to two molecules of fused paratoluidine, one molecule of zinc bromide. The temperature rose during the formation of the compound from 57° to 89°. By crystallization from alcohol a large yield of delicate white needles was obtained.

Zinc iodide, $2p\text{-}C_7H_9N.ZnI_2$.—This was formed in the same manner as the preceding, the temperature of the fused mass rising from 61° to 91°. It crystallized from alcohol in long, extremely slender white needles, having a satin luster, and forming fan-like clusters.

For other compounds, see Beilstein's Lehrbuch, p. 936.

Compounds with Orthotoluidine.

I. CADMIUM.

$2o\text{-}C_7H_9N.CdI_2$.—Formed by adding the cadmium iodide directly to the orthotoluidine. The temperature rose from 18° to 45°. It crystallized from alcohol in fan-like aggregates of soft, small needles.

II. MERCURY.

Mercuric chloride, $2o\text{-}C_7H_9N.HgCl_2$.—The temperature at moment of formation rose from 20° to 49°.5. It crystallized from alcohol in leaf-like crystals, having very much the appearance and luster of small tufts of mica.

Mercuric cyanide, $2o\text{-}C_7H_9N.HgCy_2$.—Formed similarly. Separated in beautiful crystals, with superb adamantine luster. The temperature at the moment of formation rose from 18° to 21°.

III. MANGANESE.

$2o\text{-}C_7H_9N.MnCl_2$.—Formation-temperature rose from 18° to 22°. The compound was with difficulty obtained in a pure condition from the alcoholic solution, the crystals resembling the corresponding paratoluidine compound.

IV. ZINC.

Zinc bromide, 2o-$C_7H_9N.ZnBr_2$.—The temperature of the mixed components rose from 18° to 59°, with increase of volume. Formed compact white crystalline masses.

Zinc iodide, 2o-$C_7H_9N.ZnI_2$.—The temperature rose from 17° to 58°. Tufts of fine white needles.

Compounds with Metaxylidine.

I. CADMIUM.

Cadmium bromide, $2C_8H_{11}N.CdBr_2$.—Formed in the same manner as the corresponding aniline and toluidine compounds. The temperature rose from 17° to 42°. A pinkish crystalline powder. The color was probably due to alteration in contact with the air. As first crystallized from alcohol, it was in small white needles.

Cadmium iodide, $2C_8H_{11}N.CdCl_2$.—Formation-temperature rose from 18° to 42°. Separated from alcohol in minute white crystals.

II. MERCURY.

Mercuric chloride, $2C_8H_{11}N.HgCl_3$.—The temperature rose from 18° to 71°. It crystallizes from alcohol in white needles.

Mercuric cyanide, $2C_8H_{11}N.HgCy_2$.—Minute crystals, with superb adamantine luster, and with faces apparently of a rhombohedral character.

III. ZINC.

Zinc bromide, $2C_8H_{11}N.ZnBr_2$.—The temperature rose from 17°.5 to 61°.5, with a great increase of volume. Crystallizes from alcohol in very small needles, which compact themselves together in white botryoidal masses.

Zinc iodide, $2C_8H_{11}N.ZnI_2$.—The temperature rose from 16° to 59°. Crystallizes from alcohol in small white needles, aggregated into hemispherical rosettes.

Compound with Dimethylaniline.

Mercuric chloride, $2C_6H_5(CH_3)_2N.HgCl_2$.—One molecule of mercuric chloride was added to two molecules of dimethyl-aniline, the temperature of the mixture rising from 21° to 44°. The solid mass formed on cooling was thoroughly washed with alcohol and was left as a greenish-gray powder.

Compound with Naphthylamine.

Mercuric chloride, $2C_{10}H_9N.HgCl_2$.—After fusion of the naphthylamine, and addition of the mercuric chloride, the temperature of the mixture rose from 61° to 67°. The resulting mass was washed repeatedly with alcohol without becoming white, but it crystallized from boiling ligroine in minute white needles, turning brown in contact with the air.

Note on Thiocarbanilide.

It was found that the compound $2C_6H_7N.HgCl_2$ underwent rapid decomposition when exposed in contact with carbon disulphide to the action of sunlight. Subsequently, that this decomposition took place merely by heating, and could be best effected in the following manner :

The purified chloride of diphenylmercurammonium was dissolved in alcohol, and after being mixed with carbon disulphide, was boiled for several days under a return cooler. When the reaction was finished, which was made evident by the clearing of the liquid, the precipitated HgS was filtered off, and the filtrate set aside to crystallize.

After a second crystallization, a pure product was obtained with a melting point of 144°, and which proved on analysis to be thiocarbanilide, $C_{13}H_{12}N_2S$.

	Found.	*Theory.*
Carbon	68.31	68.42
Hydrogen	5.41	5.26
Sulphur	14.00	14.04

Thiocarbotoluidide and thiocarboxylidide were formed in the same manner from $2C_7H_9N.HgCl_2$ and $2C_8H_{11}N.HgCl_2$.

The cyanide of diphenylmercurammonium also yields thiocarbanilide when boiled with carbon disulphide, hydrocyanic acid escaping.

Thiocarbanilide is ordinarily prepared by boiling aniline and alcoholic potash with an excess of carbon disulphide.

XXXV.—ANALYSIS OF BEET ROOT AND SORGHUM CANE.

BY P. CASAMAJOR.

In the United States, for the last twenty years, many attempts have been made to manufacture sugar in a commercial way, from beet root and from the sorghum cane. Such attempts continue to be made at this day, and although there is no predicting what results