These determinations were made at 23–26°. The benzene was of high purity. The average value obtained for the sample of alcohol corresponded closely to that obtained for it by the Victor Meyer method.

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DOUBLE SALTS OF ANILINE HYDROHALIDES WITH METAL HALIDES

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Aniline reacts in a great variety of ways with metallic salts to form molecular compounds, to yield oxidized and halogenated derivatives and to substitute amino or nuclear hydrogen by metal or metal–halide groups.[1] The object of this study is to review and extend the knowledge of molecular compounds of the types $n\text{An}\cdot n\text{HX}\cdot \text{MX}_n$, wherein An is aniline, X is halogen and M is metal. These and their hydrated forms are assembled in the following table. The asterisk indicates new compounds herewith contributed. The symbol of the metal is followed by its valence only where it is other than of the "ic" salt. The types of salts are arranged in the order of increasing complexity with respect to aniline hydrohalide. It will be noted that anhydrous salts are only numbered, while hydrated salts are lettered and correspondingly numbered. There are nine degrees of complexity of anhydrous salts and eight of hydrated salts, making seventeen types of complexity with respect to both aniline hydrohalide and water. In the absence of molecular weight determinations, the simplest formulas are used in the table. There is no evidence that these salts are not polymerized. For example, $\text{AnHCl}\cdot\text{HgCl}_2$ may be $(\text{AnHCl}\cdot\text{HgCl}_2)_8$.

Many of the compounds indicated by the blanks of the table were sought but could not be prepared. The known compounds, therefore, because they are most easily formed, roughly represent comparative capacities of the different metals to unite with aniline hydrohalide, their limits of capacity to enter into such union and the relative affinities of the three halogens.

As is shown in its greater number of types and its ability to form the *octo-aniline* compound, it is concluded that mercury has the greatest

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[1] See especially Whitmore's "Organic Compounds of Mercury," Chemical Catalog Company, New York, **1921**, p. 205.

TABLE I

ANHYDROUS AND HYDRATED DOUBLE SALTS

Type	Formula	Metals forming such salts where X is									
		Chlorine				Bromine				Iodine	
		M	Lit.	M	Lit	M	Lit.	M	Lit	M	Lit.
1	$AnHX\cdot 2Mx_n$	Hg	1			Hg	*			...	
2	$AnHX\cdot MX_n$	Hg	1	Mn	*	Cu^1	4	Cd	17	Hg	*
				Bi	*					Sb^3	2
						Sn^2	6	Al	18	Bi^3	23
2a	$AnHX\cdot MX_n\cdot H_2O$	Sb^3	2	Sn^2	3						
3	$4AnHX\cdot 3MX_n$					...				Pb	24
4	$3AnHX\cdot 2MX_n$	...				Al	17			Sb^3	2
5	$2AnHX\cdot MX_n$	Co	*	Sn	7	Sb^3	2	Zn	11	Zn	11
		Au	*	Fe	8	Cu^1	4	Al	18	Cd	11
		Hg	1	Te	9	Sn	6	Cd	20		
		Cu^1	4	Zn	10	Te	19	Pt	21		
		Cu	5	Cd	11						
		Sn^2	3,6	Pt	12						
5a	$2AnHX\cdot MX_n\cdot H_2O$	Fe	13	Zn	14	Zn	14			...	
5b	$2AnHX\cdot MX_n\cdot 2H_2O$	Mn	*	Fe^2	13	...				...	
				Fe	13						
5c	$2AnHX\cdot MX_n\cdot 3H_2O$	Sn	7			...				...	
6	$3AnHX\cdot MX_n$	Al	*	Bi^3	15	As	*			...	
		Sn	*								
6a	$3AnHX\cdot MX_n\cdot H_2O$	Sb^3	2			...				...	
6b	$3AnHX\cdot MX_n\cdot 2H_2O$	Zn	14			...				...	
7	$4AnHX\cdot MX_n$	Sn	6	Fe	16	Sb^3	2	Al	18	Sb^3	2
						Sn	6	Te	22		
7a	$4AnHX\cdot MX_n\cdot H_2O$	...				Sb^3	2			...	
8	$6AnHX\cdot MX_n$	Fe	13			...				...	
8b	$6AnHX\cdot MX_n\cdot 2H_2O$	Fe	13			...				...	
9	$8AnHX\cdot MX_n$	Hg	*			...				...	

(1) Swan, *Am. Chem. J.*, **20**, 613 (1898); Frank C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Company, New York, **1921**, pp. 205–210, 374; (2) Higbee, *Am. Chem. J.*, **23**, 154 (1900); (3) Slagle, *ibid.*, **20**, 663 (1898); (4) Saglier, *Compt. rend.*, **106**, 1422 (1888); (5) Destrem, *Bull. soc. chim.*, **30**, 482 (1878); (6) Richardson and Adams, *Am. Chem. J.*, **22**, 446 (1899); (7) Slagle, (3); Druce, *Chem. News*, **117**, 346 (1918); (8) McKenzie, *Am. Chem. J.*, **50**, 308 (1913); Osaka, Schima and Soshida, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **7**, 69 (1924); (9) Lenher, THIS JOURNAL, **22**, 139 (1900); (10) Tombeck, *Ann. chim.*, [7] **21**, 433 (1900); Vohl, *Dingler's polytech. J.*, **175**, 211 (1865); (11) Tombeck, (10); (12) Hofmann, *Ann.*, **47**, 62 (1843); (13) McKenzie, (8); (14) Base, *Am. Chem. J.*, **20**, 646 (1898); (15) Hauser and Vanino, *Ber.*, **33**, 2271 (1900); (16) Osaka, Schima and Soshida, (8); (17) Hjortdahl, *Z. Krist.*, **6**, 484 (1882); (18) Kablukov and Knanov, *J. Russ. Phys.-Chem. Soc.*, **41**, 1755 (1910); (19) Lenher, (9); Lowy and Dunbrook, THIS JOURNAL, **44**, 614 (1922); (20) Tombeck, (10); Hjortdahl, (17); (21) Gutbier, *Ber.*, **43**, 3228 (1910); (22) Lowy and Dunbrook, (19).

capacity of all the metals to enter into such molecular combinations.[2] Ferric halide seems to approach mercury in this respect, and other metals

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[2] This was observed also with the quinoline compounds, THIS JOURNAL, **48**, 275 (1926); **48**, 277 (1926).

in the order of lesser capacity seem to be tin, zinc and antimony. Chlorine seems to favor the greatest complexity; however, with quinoline, bromine was found to yield the greatest complexity. Iron, antimony and zinc are the most capable of forming hydrated salts with aniline hydrohalides; the bromides rarely form hydrated salts with aniline hydrohalides; the bromides rarely form hydrated salts; the iodides form none. Though magnesium bromide unites with 2, 4 and 6 moles of aniline, it could not be made to unite with aniline hydrobromide, either in hydrobromic acid or methylethyl ketone solutions.

Efforts to correlate these properties have in the past led to no certain conclusion, nor does it seem possible today to make any definite correlation.

All these compounds are double salts rather than complex salts, because they precipitate all of their halogen with silver nitrate, they liberate all of their metal with hydrogen sulfide or sulfuric acid and all of their aniline with sodium hydroxide or sodium carbonate.

That Werner's theory is inadequate to explain the constitution of these compounds[3] is especially evidenced by the existence of the iron-hexaniline compound and the octo-aniline compound of mercury. Furthermore, compounds of the table show no properties of the "inner zone."

In the preparation of heavy metal salts of the alkaloids and other bases for analytical purposes, it is usually assumed that the composition of the precipitate corresponds to Type 2, Base $HX \cdot MX_n$. That this assumption may lead to error is sufficiently indicated by this study, wherein it is especially shown that metals exercise a wide capacity to form salts of different types, under various conditions of solvent concentration, etc.

Experimental Part

In the preparation of these compounds, 0.08 mole of aniline hydrohalide and 0.01 mole of metal halide were weighed out, dissolved in the minimum amount of hot alcohol, methylethyl ketone or concentrated hydrohalogen acid, filtered and allowed to cool to room temperature. If no crystals formed, the solution was allowed to cool in a freezing mixture or the solvent evaporated spontaneously. Crystals formed were filtered out and washed with a small amount of the solvent from which they precipitated except that when too soluble the use of ether or benzene was found more satisfactory for washing. When the crystals appeared homogeneous and microscopically different from the original materials they were analyzed for metal, usually by precipitation of the sulfide. If the crystals were aniline hydrohalide or metal halide, they were re-

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[3] Recent work with other bases also shows the inadequacy of Werner's theory [Scagliarini and Monti, *Atti Accad. Lincei*, [6] **1**, 582 (1925), [6] **2**, 269 (1925); [6] **4**, 210 (1926)].

turned to the solution from which they precipitated, 0.01 mole of metal halide was added (with more solvent if necessary), the solution filtered and again allowed to crystallize. In case the double salt $4AnHX{\cdot}MX_n$ also failed to form, another 0.01 mole of metal halide was added and so on. If at any time a salt in other proportions was indicated, as, for example, Type 3, an attempt was made to prepare it directly with the calculated quantities of material.

Often the expected salt did not form but one containing proportionately less aniline hydrohalide appeared. In cases of this kind the addition of a slight excess of aniline hydrohalide or of aniline over the theoretical quantity favored the formation of the more complex double salt.

The solvent used often had a marked effect on the complexity of the double salt formed. For example, when aniline hydrochloride and cobalt chloride were dissolved in concentrated hydrochloric acid, only aniline hydrochloride precipitated, but in methylethyl ketone $2AnHCl{\cdot}CoCl_2$ was formed.

Complex types tend to decompose to more simple types with rising temperature. This was found noticeable both in preparing the salts and in determining their melting points. Thus $2An{\cdot}HgCl_2$ softens at

TABLE II

DOUBLE SALTS OF ANILINE

Composition, An = $C_6H_5NH_2$	Color, etc.	Crystal form	Softens, °C.	M. p., °C.	M, %	
					Calcd.	Found
$8AnHCl{\cdot}HgCl_2$	White	Needles	...	231.5	15.34[a]	15.42[a]
$3An{\cdot}HCl{\cdot}2HgCl_2$	Glistening	Needles[b]	160	167	46.41	46.40
$AnHBr{\cdot}2HgBr_2$	Colorless	Plates	...	156	44.83	45.11
$AnHI{\cdot}HgI_2$	Yellow	......	...	61	29.70	30.17
$2AnHCl{\cdot}CoCl_2$	Blue	......	...	135	15.16	15.48
$2AnHCl{\cdot}AuCl_3$	Golden	Prisms[c]	85	95	35.49	35.40
$AnHCl{\cdot}BiCl_3$	White	Rectangles	210 (d.)	...	45.23	44.97
$AnHCl{\cdot}MnCl_2$	White	Needles	...	...	21.51	20.60
$2AnHCl{\cdot}MnCl_2{\cdot}2H_2O$	White	Needles	...	230+	13.05	13.13
$3AnHCl{\cdot}AlCl_3$	White	Rectangles[d]	...	...	5.19	5.29
$3AnHCl{\cdot}SnCl_4$	White	Needles	...	...	18.20	18.65
$3AnHBr{\cdot}AsBi_3$	White	Powder	...	...	8.95	8.88
$An{\cdot}HgBr_2$	White	......	...	127	44.23	44.43
$An{\cdot}PbCl_2$	White	Needles[e]	...	...	55.82	56.13

[a] X, calcd., 27.11. Found: X, 27.08.

[b] Prepared in hot alcohol.

[c] On heating the hydrochloric acid solution of this salt the solution darkens and precipitates pure gold in fern-like aggregates of short prisms. The reaction appears to be similar to that observed in the case of $2An{\cdot}HgI_2$. In each the metal halide is reduced and presumably the aniline is oxidized.

[d] Prepared in a large volume of hydrochloric acid with an excess of 2 moles of aniline.

[e] Mandal, *Ber.*, **54,** 703 (1921), gives a salt, $3An{\cdot}PbCl_2$, needles easily decomposed at 20–30° or by organic solvents.

about 130° with apparent loss of aniline and the formation of An·$HgCl_2$, which then melts at 188°. In the preparation of the more complex types, the constituents were best dissolved in the minimum amount of solvent at room temperature and cooled in a freezing mixture.

Summary

Aniline exhibits a wide capacity to form compounds in combination with halogen and different metals. Seventeen types, including hydrated forms, are recognized. No correlation with properties can be made of all of these compounds on the basis of modern theories. The octo-aniline compound of mercury is easily prepared and is of special interest.

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[CONTRIBUTION FROM THE LABORATORY OF PHARMACOLOGY, THE UNIVERSITY OF CHICAGO, AND THE DEPARTMENT OF MATERIA MEDICA AND THERAPEUTICS, THE MEDICAL SCHOOL, THE UNIVERSITY OF MICHIGAN]

A METHOD FOR THE QUANTITATIVE DETERMINATION OF CYANIDE IN SMALL AMOUNTS

BY RALPH G. SMITH[1]

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The following method is the application of an established reaction in organic chemistry for the quantitative estimation of cyanide in small amounts. The method depends on the development of a reddish-brown color due to the formation of the sodium or potassium salt of isopurpuric acid, which occurs when cyanide is added to an alkaline picrate solution. In the presence of an excess of alkaline picrate the development of the color is quantitative, making it possible to estimate the amount of cyanide present colorimetrically by comparison with a standard prepared with a known amount of cyanide.

Durien[2] applied such a method for the quantitative estimation of hydrocyanic acid in bitter almond water. Runne,[3] in a survey of the quantitative methods for the determination of cyanide, established the procedure of Durien as accurate to within one per cent. Waller[4] used a similar method in the analysis of tissue distillates for hydrocyanic acid. From a stock solution of alkaline picrate containing a definite amount of cyanide, color standards are prepared with which the unknown solution is compared. Furthermore, as Waller has pointed out, the reaction has been described previously as a qualitative test for cyanide, by various workers.[5]

[1] Fellow in Medicine of the National Research Council.

[2] Durien, *Jahresb. Pharm.*, **37**, 439 (1902).

[3] Runne, *Apoth.-Ztg.*, **24**, 357 (1909).

[4] Waller, *J. Physiol.*, **40** (Proceedings of the Physiological Society, June 18) (1910).

[5] Hlasiwetz, *Ann.*, **110**, 289 (1859); Reichardt, *Chem.-Ztg.*, **25**, 537 (1901); Guignard, *Ann. sci. pharmacol.*, 415 (1906).