ART. XLI.—*On the Ammonium-Cuprous Double Halogen Salts;* by H. L. WELLS and E. B. HURLBURT.

THE existence of ammonium-cuprous double halides has long been known, but since no complete investigation of these compounds had been made, a careful study of them has been undertaken.

Mitscherlich* prepared the potassium salt, $4KCl \cdot Cu_2Cl_2$, and mentioned the corresponding ammonium salt. This salt, $4NH_4Cl \cdot Cu_2Cl_2$, has been obtained in the present investigation.

Deherain† described three double chlorides, $4NH_4Cl \cdot Cu_2Cl_2 \cdot H_2O$, $2NH_4Cl \cdot Cu_2Cl_2$ and $NH_4Cl \cdot Cu_2Cl_2$. The first of these salts, if the molecule of water is omitted, corresponds to the compound mentioned by Mitscherlich which we have

* Ann. Chim. Phys., lxxiii, 384. † Comptes Rendus, lv, 808.

obtained, and we are convinced that Deherain's formula for it is wrong. The second salt, $2NH_4Cl . Cu_2Cl_2$, has not been obtained by us, but since it corresponds in type to a bromide and an iodide which are easily prepared, its existence seems possible. The third salt of Deherain, $NH_4Cl . Cu_2Cl_2$, probably does not exist, for we have failed to obtain it, as has Ritthausen also. Ritthausen,* while not being able to prepare $NH_4Cl . Cu_2Cl_2$, obtained the compound $4NH_4Cl . 3Cu_2Cl_2$, and we have confirmed this result. The compositions required for the two formulæ do not differ widely, so that it is probable that Deherain analyzed the salt $4NH_4Cl . 3Cu_2Cl_2$ and gave it an incorrect formula.

As far as we know, no double bromides have been previously described. Saglier† has described an ammonium-cuprous iodide, to which the formula $2NH_4I . Cu_2I_2 . H_2O$ is given. The single double iodide which we have obtained corresponds to Saglier's description and to his formula, except that we have found it to be undoubtedly anhydrous.

In the present investigation a great number of experiments have been made, with gradually varying proportions of the constituent salts in each case, in order to obtain as many compounds as possible.

The Chlorides, $4NH_4Cl . Cu_2Cl_2$ and $4NH_4Cl . 3Cu_2Cl_2$.— These compounds were prepared by making hot hydrochloric acid solutions of mixtures of the simple salts, usually in the presence of copper wire, and cooling to crystallization. The first salt mentioned above is very readily oxidized by exposure to air, hence it has been found advisable in making it to use a flask and to protect the solution from air by means of a stream of carbonic acid.

The compound $4NH_4Cl . Cu_2Cl_2$ requires the presence of a comparatively large amount of ammonium chloride for its formation and crystallizes in colorless prisms which rapidly change in color through brown to green upon exposure to the air. Crystals 20^{mm} in length and 5^{mm} in thickness were observed.

The following analyses of two separate crops were made:

			Calculated for $4NH_4Cl . Cu_2Cl_2$.
Ammonium	17·91	18·12	17·48
Copper	29·69	29·28	30·79
Chlorine	50·66	50·37	51·73
	98·26	97·77	100·00

* J. pr. Ch., lix, 369. † Comptes Rendus, civ, 1440.

It was necessary to dry the samples for analysis very rapidly on account of their instability, and some water was unavoidably left in them, causing the low summations. The amount of water corresponding to one molecule (Deherain's formula) is 4·19 per cent.

The other chloride, $4NH_4Cl \cdot 3Cu_2Cl_2$, is produced when the simple salts are mixed in the required proportion in hydrochloric acid solution, and also under considerable variations from these proportions. It forms brilliant, colorless dodecahedrons which are moderately stable in the air at ordinary temperatures, but gradually turn green on exposure.

The following analyses of three separate crops were made:

	I.	II.	III.	Calculated for $4NH_4Cl \cdot 3Cu_2Cl_2$.
Ammonium	9·39	9·73	9·73	8·92
Copper	47·19	46·73	46·79	47·15
Chlorine	42·81	43·11	43·13	43·93
	99·39	99·57	99·65	100·00

The calculated amounts of ammonium, copper and chlorine for Deherain's formula, $NH_4Cl \cdot Cu_2Cl_2$, are 7·15, 50·50 and 42·35 respectively, and it does not seem possible that this formula represents the true composition of the salt, because the samples analyzed were well crystallized and evidently very pure.

The Bromides, $4NH_4Br \cdot Cu_2Br_2$ and $2NH_4Br \cdot Cu_2Br_2 \cdot H_2O$.—By the use of ammonium bromide, cuprous bromide, hydrobromic acid and copper wire, these compounds were produced similarly to the chlorides, but since these salts oxidize much less readily than the chlorides, no protection by means of carbon dioxide was necessary in any case.

The first salt, $4NH_4Br \cdot Cu_2Br_2$, is formed in the presence of an excess of ammonium bromide and resembles the corresponding chloride in form, occurring in long, colorless prisms which turn green after long exposure to the air. Analyses of two separate crops gave:

	I.	II.	Calculated for $4NH_4Br \cdot Cu_2Br_2$.
Ammonium	10·24	10·24	10·61
Copper	18·81	18·47	18·68
Bromine	70·93	70·60	70·71
	99·98	99·31	100·00

The other bromide, $2NH_4Br \cdot Cu_2Br_2 \cdot H_2O$, is formed in the presence of a relatively greater amount of cuprous bromide. It forms brilliant, colorless rhombohedrons, sometimes 15^{mm}

long and 9mm wide, and it is more stable in the air than the first bromide. Analyses of two separate crops gave:

	I.	II.	Calculated for $2NH_4Br . Cu_2Br_2 . H_2O$.
Ammonium	6·88	6·90	7·19
Copper	25·61	25·20	25·32
Bromine	63·76	64·08	63·90
Water (difference)	3·75	3·82	3·59

The Iodide, $2NH_4I . Cu_2I_2$.—Only one double iodide could be obtained by the use of ammonium iodide and cuprous iodide in widely varying proportions in hydroiodic acid solutions. This circumstance agrees with the observation made upon several other series of double salts studied in this laboratory, that the number of double salts possible decreases from the chlorides to the iodides. Two separate crops gave the following results upon analysis:

	I.	II.	Calculated for $2NH_4I . Cu_2I_2$.
Ammonium	5·84	5·95	5·36
Copper	18·75	----	18·90
Iodine	75·07	75·55	75·74
	99·66		100·00

Summary.—The double salts obtained in the present investigation are as follows:

2 : 1 Type.	1 : 1 Type.	2 : 3 Type.
$4NH_4Cl . Cu_2Cl_2$	----------	$4NH_4Cl . 3Cu_2Cl_2$
$4NH_4Br . Cu_2Br_2$	$2NH_4Br . Cu_2Br_2 . H_2O$	----------
----------	$2NH_4I . Cu_2I_2$	----------

The two bromides are apparently new compounds, while a formula without water has been given to Saglier's iodide. The compound, $NH_4Cl . Cu_2Cl_2$, of Deherain probably does not exist.

It was hoped that ammonium-cuprous salts of other types, corresponding to the cæsium-cuprous salts described by one of us* would be found, but such has not been the case, and there is no correspondence between the two series. The view advanced in the article just mentioned, that the formula $4NH_4Cl . 3Cu_2Cl_2$ might be considered somewhat doubtful on account of its complexity and because its variation from the 1 : 2 type is slight, seems to have been unfounded.

Sheffield Scientific School, New Haven, Conn., June, 1895.

*This Journal, xlvii, 96.