CLVI. NEUTRAL SALT ADDITION COMPOUNDS OF *N*-METHYLATED GLYCINES: THEIR FORMULATION AND THAT OF THEIR HYDRATES.

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(Received August 31st, 1928.)

It is now a well-established fact that some of the naturally occurring α -amino-acids have the property of forming addition compounds with neutral salts, such as the halides of the alkali and alkaline earth metals. It is probable that all exhibit this property to some extent in solution, but the isolation of crystalline additive products is only successful where the solubility of the addition product is less than that of the amino-acid or the inorganic salt, a condition of infrequent occurrence.

Glycine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, furnishes the best example of an extended series of addition compounds [Pfeiffer and Modelski, 1912, 1913; King and Palmer, 1920] and its simple derivatives sarcosine, $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, alanine, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, and betaine, $\text{NMe}_3^+ \cdot \text{CH}_2 \cdot \text{CO}_2^-$, have supplied a few further instances of this additive property [Pfeiffer, 1922].

The aim of the present investigation was primarily the use of *N*-dimethyl-aminoacetic acid, $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, where the glycine type is retained, but where there are no longer any hydrogen atoms attached to nitrogen. This acid has given a particularly complete series of additive compounds with the chlorides, bromides and iodides of calcium, strontium, barium, lithium and sodium, but only one compound with a potassium halide. The composition of these complexes when compared with those, so far as they were known, of glycine, sarcosine and betaine revealed such striking analogies that the preparation of the missing additive compounds of sarcosine and betaine was also undertaken.

The complete series of additive compounds of glycine and its mono-, di-, and tri-methyl-derivatives is shown in the following table where G = glycine, S = sarcosine, D = dimethylglycine and B = betaine (anhydrous).

With one exception, all of these compounds belong to one of four types. They contain a metallic salt associated with 1, 2, 3 or 4 molecules of the amino-acid and for such there is only one consistent interpretation of their structure. The inorganic components are highly ionised salts and there is

Glycine	Sarcosine	Dimethylglycine	Betaine
G. CaCl ₂ .3H ₂ O ^a	S. CaCl ₂ .4H ₂ O ^b	D. CaCl ₂ .4H ₂ O ^c	—
G ₂ . CaCl ₂ .4H ₂ O ^{a, c, d}	—	—	—
G ₃ . CaCl ₂ ^a	S ₃ . CaCl ₂ ^b	—	—
G ₂ . CaBr ₂ .4H ₂ O ^{a, d}	—	D ₂ . CaBr ₂ .6H ₂ O ^e	—
G ₃ . CaBr ₂ ^d	S ₃ . CaBr ₂ ^e	—	—
G ₂ . CaI ₂ .3H ₂ O ^{c, d}	S ₂ . CaI ₂ .3H ₂ O ^e	D. CaI ₂ ^e	B ₅ . (CaI ₂) ₂ .11H ₂ O ^e
G ₄ . CaI ₂ ^d	—	—	—
G ₂ . SrCl ₂ .H ₂ O ^c	S. SrCl ₂ .4H ₂ O ^{b, e}	D. SrCl ₂ .4H ₂ O ^e	B. SrCl ₂ .4H ₂ O ^e
G ₂ . SrCl ₂ .3H ₂ O ^a	—	—	—
G ₂ . SrBr ₂ .3H ₂ O ^a	S. SrBr ₂ .4H ₂ O ^e	D. SrBr ₂ .4H ₂ O ^e	B. SrBr ₂ .5H ₂ O ^e
G ₄ . SrI ₂ ^d	S ₃ . SrI ₂ .2H ₂ O ^d	D ₂ . SrI ₂ .3H ₂ O ^e	B ₃ . SrI ₂ .4H ₂ O ^e
—	S. SrI ₂ .4H ₂ O ^e	—	—
G ₂ . BaCl ₂ .H ₂ O ^{a, c}	S. BaCl ₂ .4H ₂ O ^b	D. BaCl ₂ .4H ₂ O ^e	B. BaCl ₂ .4H ₂ O ^a
—	S. BaBr ₂ .4H ₂ O ^b	D. BaBr ₂ .4H ₂ O ^e	B. BaBr ₂ .4H ₂ O ^a
G ₂ . BaBr ₂ .H ₂ O ^a	—	—	B ₂ . BaBr ₂ .6H ₂ O ^b
G ₄ . BaI ₂ ^d	S ₂ . BaI ₂ .2H ₂ O ^e	D ₂ . BaI ₂ .4H ₂ O ^e	B. BaI ₂ .4H ₂ O ^e
G. LiCl.H ₂ O ^{a, c}	S. LiCl.H ₂ O ^{d, e}	D. LiCl.2H ₂ O ^e	—
G ₂ . LiCl.H ₂ O ^a	—	—	—
G. LiBr.H ₂ O ^{a, c}	S. LiBr.H ₂ O ^{d, e}	D. LiBr.H ₂ O ^e	B. LiBr.2½H ₂ O ^e
G ₂ . LiBr.H ₂ O ^{a, c}	—	D ₂ . LiBr ^e	—
G. LiI.H ₂ O ^d	S. LiI.1½H ₂ O ^{d, e}	D. LiI.6H ₂ O ^e	B ₂ . LiI.H ₂ O ^e
—	S. NaCl.H ₂ O ^d	D. NaCl.2H ₂ O ^e	B. NaCl.1½H ₂ O ^e
G. NaBr.1½H ₂ O ^d	S. NaBr.H ₂ O ^d	D. NaBr.H ₂ O ^e	—
G ₂ . NaBr.H ₂ O ^c	—	D ₂ . NaBr.2H ₂ O ^e	B ₂ . NaBr.1½H ₂ O ^e
G ₂ . NaI.H ₂ O ^{c, d}	S. NaI.H ₂ O ^{b, d}	D. NaI.3H ₂ O ^e	B. NaI.2H ₂ O ^e
—	S ₃ . KCl.5H ₂ O ^e	—	—
—	S ₄ . KBr.4H ₂ O ^{b, e}	—	B. KBr.2H ₂ O ^a
G ₄ . KI ₃ ^d	S ₃ . KI ₃ ^d	D. KI.1½H ₂ O ^e	B. KI.2H ₂ O ^a
—	S ₄ . KI.4H ₂ O ^b	—	B ₂ . KI.2H ₂ O ^a

^a Pfeiffer and Modelski [1912].^b Pfeiffer and Wittka [1915].^c King and Palmer [1920].^d Pfeiffer, Klossmann and Angern [1924].^e Anslow and King (this paper).

little doubt that they remain so in these complexes and are held by electrovalencies. The metallic cations are free to co-ordinate with the carboxyl oxygen atoms of the amino-acid molecules, two of the four electrons of the carbonyl oxygen atom entering the outer shell of the metallic cation in the manner suggested for the neutral salt addition compounds of alkaline earth glutamates and aspartates by Anslow and King [1927]. The compounds with sarcosine or glycine, for instance, where all four types are observed will have the general structure

where M is the metallic cation co-ordinated through carbonyl oxygen to 1, 2, 3 or 4 amino-acid molecules and X is the halogen ion, the number, 1 or 2, depending on the electro-valency of M. On no other formulation, such for example as the combination of the halogen ion with the ammonium form of the amino-acid, does it seem possible to interpret such complexes as triglycine calcium bromide prepared by Pfeiffer, Klossmann and Angern [1924] or its sarcosine analogue, trisarcosine calcium bromide prepared by us.

So far, the formulation of the amino-acid molecules in their relation to the metallic atoms has been discussed to the exclusion of the water molecules.

The electronic arrangement of the oxygen atom in water is, however, similar to that of the carbonyl oxygen atom and the composition of the addition compounds formed between dimethylglycine and lithium bromide, $D.LiBr.H_2O$ and $D_2.LiBr$, and between sarcosine and the potassium halides, $S_3.KCl.5H_2O$, $S_4.KBr.4H_2O$ and $S_4.KI.4H_2O$, even suggests inter-equivalence in these cases of amino-acid and water molecules. If, therefore, the view be accepted that these additive compounds are held together by co-valencies, then in a series of about eighty compounds such as are enumerated here, one might by a consideration of the number of water molecules expect to find examples where the known maximum co-ordination number of the metallic element is exhibited. Such indeed is the case. Consider, for example, the additive compounds of dimethylglycine. The majority of the alkaline earth halide addition compounds are hydrated and most of them may be formulated as having a co-ordination number of 6. The commonest type is $D.MX_2.4H_2O$ and this falls into the scheme if each oxygen atom of the carboxyl group occupies one position in the co-ordination complex. Thus, dimethylglycine calcium chloride tetrahydrate would be written

whilst the type exemplified by di-dimethylglycine barium iodide tetrahydrate would be written

The exceptional hexahydration observed with di-dimethylglycine calcium bromide hexahydrate suggests either a co-ordination number of 8 for calcium as postulated by Pfeiffer in $[\text{Ca}(\text{NH}_3)_8]\text{Cl}_2$ or attachment of the extra water molecules to the tertiary nitrogen atoms, one to each.

In a similar way the hydrates of the alkali halide addition compounds of dimethylglycine, with the exception of that with lithium iodide, may be formulated on the basis of a co-ordination number of 2 or 4 for the alkali metal. The same principles apply to the majority of the compounds of glycine, sarcosine and betaine.

One or two cases call for further comment. The exceptional series of compounds formed between sarcosine and the potassium halides mentioned above are most simply interpreted on a co-ordination number of 8 for potassium, the interchange of water and amino-acid molecules, and the odd number of amino-acid and water molecules in $S_3.KCl.5H_2O$, being difficult to account for in any other way.

If the above views are correct, they ought to account for the most remarkable compound of this series yet observed. Betaine and calcium iodide form a well-authenticated addition compound containing eleven molecules of

water, $B_5 \cdot (CaI_2)_2 \cdot 11H_2O$. It crystallises in the cubic system and is optically isotropic. This is formulated as

where B is the hydrated form of betaine and calcium has the usual co-ordination number of 6. The use of betaine as a bridge between the two calcium atoms involves the use of both oxygen atoms of the carboxyl group, each occupying one co-ordination position of a calcium atom, and thus strengthens the formulation proposed above for the commonest type of compound observed between dimethylglycine and the alkaline earth halides, $D \cdot MX_2 \cdot 4H_2O$.

EXPERIMENTAL.

Addition compounds of N-methylaminoacetic acid (sarcosine).

Tri-sarcosine calcium bromide. Sarcosine hydrobromide (4.25 g.) was boiled with excess of calcium hydroxide; after treatment with carbon dioxide the solution was boiled, filtered and concentrated. On keeping, large, well-formed, rectangular plates were obtained (1.0 g.). These were filtered off rapidly, transferred to porous plate and well pressed to remove all adhering mother-liquor. (This method was used for all the addition compounds.)

0.2086 g.; 0.1717 g. AgBr. Br = 35.0 %.

0.1902 g.; NH_3 = 14.48 cc. $N/10$ acid. N = 8.5 %.

Calc. for $(C_2H_7O_2N)_3 \cdot CaBr_2$; Br = 34.3 %; N = 9.0 %.

Di-sarcosine calcium iodide trihydrate. Square plates (1.9 g.) were obtained in the usual way from sarcosine hydriodide (4.3 g.) and excess calcium hydroxide. (Found: I, 48.1; N, 6.7 %; whence I : N = 1 : 1.26.) Recrystallisation gave elongated rectangular plates (0.5 g.) of the pure compound.

0.1720 g.; 0.1540 g. AgI. I = 48.4 %.

0.1740 g.; NH_3 = 6.45 cc. $N/10$ acid. N = 5.2 %.

Calc. for $(C_2H_7O_2N)_2 \cdot CaI_2 \cdot 3H_2O$; I = 48.2 %; N = 5.3 %.

Di-sarcosine barium iodide dihydrate. Prepared in a similar way to the previous compound, this *dihydrate* crystallised in needles (0.9 g.).

0.2090 g.; 0.1607 g. AgI. I = 41.6 %.

0.2070 g.; NH_3 = 6.53 cc. $N/10$ acid. N = 4.4 %.

Calc. for $(C_2H_7O_2N)_2 \cdot BaI_2 \cdot 2H_2O$; I = 41.9 %; N = 4.6 %.

Sarcosine strontium chloride tetrahydrate. This compound, previously prepared by Pfeiffer and Wittka [1915] from equimolecular solution, was obtained in needles from a solution of sarcosine and strontium chloride in the ratio 2 : 1. (Found: Cl, 21.7; N, 4.4 %. Theory: Cl, 22.2; N, 4.4 %.)

Sarcosine strontium bromide tetrahydrate. Needles (1.4 g.) were obtained in the usual manner.

0.2006 g. dried at 120° lost 0.0336 g. H_2O = 16.8 %.

0.2006 g.; 0.1810 g. AgBr. Br = 38.4 %.

0.2039 g.; NH_3 = 5.36 cc. $N/10$ acid. N = 3.7 %.

Calc. for $C_2H_7O_2N \cdot SrBr_2 \cdot 4H_2O$; H_2O = 17.6 %; Br = 39.1 %; N = 3.4 %.

Sarcosine strontium iodide tetrahydrate. Concentration of a solution prepared in the usual way gave needles (1.2 g.) which were impure. (Found: I, 48.2; N, 3.3 %; whence I : N = 1 : 0.62.) When, however, an equimolecular solution was concentrated needles (1.3 g.) of the pure compound were obtained.

0.2022 g.; 0.1872 g. AgI. I = 50.0 %.

0.2082 g.; NH_3 = 4.10 cc. *N*/10 acid. N = 2.8 %.

Calc. for $\text{C}_3\text{H}_7\text{O}_2\text{N} \cdot \text{SrI}_2 \cdot 4\text{H}_2\text{O}$; I = 50.5 %; N = 2.8 %.

Tri-sarcosine potassium chloride pentahydrate. Sarcosine hydrochloride (4.2 g.) was dissolved in 33.3 cc. *N* potassium hydroxide and the solution concentrated. After the removal of potassium chloride (1.1 g.), well-formed hexagonal plates were deposited (0.4 g.).

0.2080 g.; 0.0661 g. AgCl. Cl = 7.9 %.

0.1885 g.; NH_3 = 13.04 cc. *N*/10 acid. N = 9.7 %.

Calc. for $(\text{C}_3\text{H}_7\text{O}_2\text{N})_3 \cdot \text{KCl} \cdot 5\text{H}_2\text{O}$; Cl = 8.2 %; N = 9.7 %.

The existence of the tetra-sarcosine potassium bromide tetrahydrate of Pfeiffer and Wittka [1915] and of sarcosine lithium chloride monohydrate, sarcosine lithium bromide monohydrate and sarcosine lithium iodide sesquihydrate of Pfeiffer, Klossmann and Angern [1924] was confirmed.

Salts of N-dimethylaminoacetic acid.

N-Dimethylaminoacetic acid hydrochloride. This compound, described by Johnson [1906] and Friedmann [1908], was prepared by slowly dropping an aqueous solution of monochloroacetic acid (8.25 g. in 8.2 cc.) into a solution of dimethylamine (100 cc., 16.5 % aq.) cooled to 0°, followed by four hours' heating in a pressure bottle at 55°. An excess of baryta was added on cooling, and the liberated dimethylamine removed by concentration *in vacuo*. After exact precipitation of the barium by sulphuric acid and removal of the barium sulphate, concentration to a small volume (at 50°), followed by the addition of an equal volume of alcohol, gave a mass of transparent tablets, melting at 189–191°. The total yield was 8.75 g. (Found: Cl = 25.6 %. Theory: 25.2 %.)

The free acid was prepared by adding to a solution of the hydrochloride a slight excess of silver carbonate; after removal of the excess of silver with hydrogen sulphide, concentration gave very hygroscopic tablets which were dried *in vacuo* over sulphuric acid. This acid is readily soluble in dry methyl alcohol, but crystallises well in sheaves of needles on careful addition of acetone. M.P. 176–178° (Johnson gives M.P. 157–160°). (Found: N = 13.3 %. Theory: 13.6 %.)

The *chloroaurate* is dimorphous and very readily soluble in water. The less stable form separates as a microcrystalline pale yellow powder on concentration and in contact with the solution soon changes into deep orange rhombs. M.P. 96–98°.

0.1131 g. dried at 90° lost 0.0039 g. H_2O = 3.4 %.

0.1399 g.; 0.0587 g. Au. Au = 42.0 %.

Calc. for $\text{C}_4\text{H}_9\text{O}_2\text{N} \cdot \text{HAuCl}_4 \cdot \text{H}_2\text{O}$; H_2O = 3.9 %; Au = 42.8 %.

N-Dimethylaminoacetic acid hydrobromide. Prepared by concentrating a solution of the amino-acid containing excess hydrobromic acid, this salt was obtained in anhydrous, elongated hexagonal plates which are slightly hygroscopic; it is less soluble than the hydrochloride. M.P. 158–160°.

0.2013 g.; 0.2053 g. AgBr. Br = 43.4 %.

Calc. for $C_4H_9O_2N \cdot HBr$; Br = 43.4 %.

N-Dimethylaminoacetic acid hydriodides. The *monohydriodide*, prepared in a similar way to the hydrobromide, crystallises in hexagonal plates which are anhydrous and melt at 149°. Solutions become coloured on heating.

0.1964 g.; 0.1981 g. AgI. I = 54.5 %.

Calc. for $C_4H_9O_2N \cdot HI$; I = 54.9 %.

The *semi-hydriodide*, prepared by using less hydriodic acid, concentrating to a small volume and adding alcohol until turbid, crystallised on standing overnight in tufts of broad needles. The recrystallised compound (a *monohydrate*) melts at 157°, but is decomposed if heated to 120° for half an hour.

0.2017 g.; 0.1326 g. AgI. I = 35.5 %.

0.2040 g.; NH_3 = 11.94 cc. $N/10$ acid. N = 8.2 %.

Calc. for $(C_4H_9O_2N)_2 \cdot HI \cdot H_2O$; I = 36.1 %; N = 8.0 %.

Attempts to prepare the semi-hydrochloride and semi-hydrobromide were unsuccessful—the less soluble normal salts contaminating the products obtained in each case, even after recrystallisation.

Addition compounds of N-dimethylaminoacetic acid.

N-Dimethylaminoacetic acid calcium chloride tetrahydrate. *N-Dimethylaminoacetic acid hydrochloride* (4.8 g.) dissolved in a small volume of water was boiled with excess of calcium hydroxide. Carbon dioxide was passed to remove the excess, and the solution was boiled to decompose carbamates, filtered and concentrated. After standing several days the syrupy solution deposited prismatic rods (1.25 g.).

0.2103 g. dried at 120° lost 0.0502 g. H_2O = 23.9 %.

0.2103 g.; 0.2050 g. AgCl. Cl = 24.1 %.

0.1951 g.; NH_3 = 7.03 cc. $N/10$ acid. N = 5.0 %.

Calc. for $C_4H_9O_2N \cdot CaCl_2 \cdot 4H_2O$; H_2O = 25.1 %; Cl = 24.8 %; N = 4.9 %.

Di-(N-dimethylaminoacetic acid) calcium bromide hexahydrate. *N-Dimethylaminoacetic acid hydrobromide* (6.1 g.) was boiled with excess calcium hydroxide in a similar way to the previous compound; 0.75 g. of long rods were obtained. This hexahydrate on drying loses $4H_2O$ at 120° and a further $\frac{1}{2}H_2O$ at 160°.

0.1945 g. dried at 120° lost 0.0271 g. H_2O = 13.9 %.

0.1500 g. dried at 160° lost 0.0239 g. H_2O = 15.9 %.

0.1945 g.; 0.1445 g. AgBr. Br = 31.6 %.

0.1993 g.; NH_3 = 7.43 cc. $N/10$ acid. N = 5.2 %.

Calc. for $(C_4H_9O_2N)_2 \cdot CaBr_2 \cdot 6H_2O$; $4H_2O$ = 14.0 %; $\frac{1}{2}H_2O$ = 15.8 %; Br = 31.1 %; N = 5.4 %.

A second less pure crop was obtained crystallising in needles.

N-Dimethylaminoacetic acid calcium iodide. *N*-Dimethylaminoacetic acid hydriodide (5.8 g.) was boiled with excess calcium hydroxide, and treated in the usual way; the solution deposited long needles (0.7 g.).

0.1937 g.; 0.1692 g. AgI. I=47.2 %.

0.2022 g.; NH_3 =7.40 cc. *N*/10 acid. N=5.1 %.

Calc. for $\text{C}_4\text{H}_9\text{O}_2\text{N} \cdot \text{CaI}_2$; I=47.0 %; N=5.2 %.

N-Dimethylaminoacetic acid barium chloride tetrahydrate. Prepared under the foregoing conditions, long needles (0.9 g.) were obtained.

0.2003 g. dried at 120° lost 0.0391 g. H_2O =19.3 %.

0.2003 g.; 0.1464 g. AgCl. Cl=18.1 %.

0.2057 g.; NH_3 =5.78 cc. *N*/10 acid. N=3.9 %.

Calc. for $\text{C}_4\text{H}_9\text{O}_2\text{N} \cdot \text{BaCl}_2 \cdot 4\text{H}_2\text{O}$; H_2O =18.8 %; Cl=18.5 %; N=3.7 %.

A further crop was obtained on concentration.

N-Dimethylaminoacetic acid barium bromide tetrahydrate. Long needles (2.0 g.) were obtained under similar conditions.

0.2079 g. dried at 120° lost 0.0315 g. H_2O =15.2 %.

0.2079 g.; 0.1634 g. AgBr. Br=33.5 %.

0.2017 g.; NH_3 =4.61 cc. *N*/10 acid. N=3.2 %.

Calc. for $\text{C}_4\text{H}_9\text{O}_2\text{N} \cdot \text{BaBr}_2 \cdot 4\text{H}_2\text{O}$; H_2O =15.3 %; Br=33.8 %; N=3.0 %.

Di-(*N*-dimethylaminoacetic acid) barium iodide tetrahydrate. This compound was obtained in needles (0.6 g.) after recrystallisation of a slightly impure crop (1.6 g.) obtained in the usual way.

0.1943 g. dried at 120° lost 0.0186 g. H_2O =9.6 %.

0.1943 g.; 0.1338 g. AgI. I=37.2 %.

0.1969 g.; NH_3 =5.32 cc. *N*/10 acid. N=3.8 %.

Calc. for $(\text{C}_4\text{H}_9\text{O}_2\text{N})_2 \cdot \text{BaI}_2 \cdot 4\text{H}_2\text{O}$; H_2O =10.8 %; I=37.9 %; N=4.2 %.

N-Dimethylaminoacetic acid strontium chloride tetrahydrate. On concentration of an aqueous solution prepared in the usual way, this compound crystallised as a network of needles (2.6 g.).

0.1943 g. dried at 120° lost 0.0425 g. H_2O =21.9 %.

0.1943 g.; 0.1606 g. AgCl. Cl=20.5 %.

0.2023 g.; NH_3 =6.18 cc. *N*/10 acid. N=4.3 %.

Calc. for $\text{C}_4\text{H}_9\text{O}_2\text{N} \cdot \text{SrCl}_2 \cdot 4\text{H}_2\text{O}$; H_2O =21.6 %; Cl=21.2 %; N=4.2 %.

The mother-liquors gave a second crop on concentration.

N-Dimethylaminoacetic acid strontium bromide tetrahydrate. Under the foregoing conditions, long rods (2.9 g.) were obtained.

0.2035 g. dried at 120° lost 0.0335 g. H_2O =16.5 %.

0.2035 g.; 0.1784 g. AgBr. Br=37.3 %.

0.1951 g.; NH_3 =5.24 cc. *N*/10 acid. N=3.8 %.

Calc. for $\text{C}_4\text{H}_9\text{O}_2\text{N} \cdot \text{SrBr}_2 \cdot 4\text{H}_2\text{O}$; H_2O =17.0 %; Br=37.8 %; N=3.3 %.

A further crop was obtained on concentration.

Di-(*N*-dimethylaminoacetic acid) strontium iodide trihydrate. On concentration of a solution obtained in the usual way, a first crop (0.8 g.) was obtained slightly impure. (Found: H_2O , 9.2; I, 37.6; N, 4.8 %; whence I : N = 1 : 1.16.) The second crop gave more correct figures:

0.1977 g. dried at 120° lost 0.0179 g. H_2O =9.1 %.

0.1977 g.; 0.1518 g. AgI. I=41.5 %.

0.1792 g.; NH_3 =6.07 cc. *N*/10 acid. N=4.7 %.

Calc. for $(\text{C}_4\text{H}_9\text{O}_2\text{N})_2 \cdot \text{SrI}_2 \cdot 3\text{H}_2\text{O}$; H_2O =9.0 %; I=42.2 %; N=4.7 %.

N-Dimethylaminoacetic acid lithium chloride dihydrate. *N*-Dimethylaminoacetic acid hydrochloride (4.8 g.) was boiled with lithium carbonate (1 mol.); concentration gave bold tablets (3.3 g.).

0.1973 g. dried at 120° lost 0.0388 g. $H_2O = 19.7\%$.

0.1973 g.; 0.1547 g. AgCl. $Cl = 19.7\%$.

0.2002 g.; $NH_3 = 11.12$ cc. *N*/10 acid. $N = 7.8\%$.

Calc. for $C_4H_9O_2N \cdot LiCl \cdot 2H_2O$; $H_2O = 19.9\%$; $Cl = 19.5\%$; $N = 7.7\%$.

N-Dimethylaminoacetic acid lithium bromide monohydrate and di-(*N*-dimethylaminoacetic acid) lithium bromide. When an equimolecular solution of *N*-dimethylaminoacetic acid and lithium bromide was concentrated, long needles (1.3 g.) were obtained, which corresponded approximately to the compound $C_4H_9O_2N \cdot LiBr \cdot 1\frac{1}{2}H_2O$ (Found: H_2O , 11.5; Br, 35.2; N, 6.7%; whence Br : N = 0.92 : 1); whilst on further concentration a crop of tablets (0.25 g.) of quite distinct appearance separated, approximating to the formula $(C_4H_9O_2N)_2 \cdot LiBr$. (Found: Br, 28.6; N, 9.1%; whence Br : N = 1.1 : 2.)

To isolate each of these two compounds in a pure condition, separate solutions containing lithium bromide and *N*-dimethylaminoacetic acid in the proportion of 2 : 1 and 1 : 2 were concentrated. The solution containing excess lithium bromide deposited rectangular plates (2.0 g.) which were deliquescent.

0.2078 g. dried at 120° lost 0.0212 g. $H_2O = 10.2\%$.

0.2078 g.; 0.1846 g. AgBr. $Br = 37.8\%$.

0.1970 g.; $NH_3 = 9.79$ cc. *N*/10 acid. $N = 7.0\%$.

Calc. for $C_4H_9O_2N \cdot LiBr \cdot H_2O$; $H_2O = 8.7\%$; $Br = 38.4\%$; $N = 6.7\%$.

The second solution, containing two molecular proportions of *N*-dimethylaminoacetic acid, deposited hexagonal tablets (0.3 g.).

0.1212 g.; 0.0794 g. AgBr. $Br = 27.9\%$.

0.1457 g.; $NH_3 = 9.80$ cc. *N*/10 acid. $N = 9.4\%$.

Calc. for $(C_4H_9O_2N)_2 \cdot LiBr$; $Br = 27.3\%$; $N = 9.5\%$.

N-Dimethylaminoacetic acid lithium iodide hexahydrate. An equimolecular solution of lithium iodide and *N*-dimethylaminoacetic acid on concentration either on the water-bath or at room temperature, deposited mixed crystals. (Found in different preparations = I : N = 1 : 1.2.)

On this basis a third solution containing lithium iodide and *N*-dimethylaminoacetic acid in the proportion of 2 : 1 was concentrated at room temperature and gave rods (1.0 g.).

0.2112 g.; 0.1411 g. AgI. $I = 36.1\%$.

0.2060 g.; $NH_3 = 6.02$ cc. *N*/10 acid. $N = 4.1\%$.

Calc. for $C_4H_9O_2N \cdot LiI \cdot 6H_2O$; $I = 36.8\%$; $N = 4.1\%$.

Di-(*N*-dimethylaminoacetic acid) sodium chloride dihydrate. After several unsuccessful attempts with 1 : 1 solutions, this compound was obtained crystallising in irregular octahedra from a solution containing two molecules of *N*-dimethylaminoacetic acid to one of sodium chloride by evaporation in a desiccator over sulphuric acid. It gradually decomposes when dried at 120°.

0.1981 g.; 0.0995 g. AgCl. $Cl = 12.4\%$.

0.1946 g.; $NH_3 = 12.67$ cc. *N*/10 acid. $N = 9.1\%$.

Calc. for $(C_4H_9O_2N)_2 \cdot NaCl \cdot 2H_2O$; $Cl = 11.8\%$; $N = 9.3\%$.

N-Dimethylaminoacetic acid sodium bromide monohydrate and di-(*N*-dimethylaminoacetic acid) sodium bromide sesquihydrate. Concentration of an equimolecular solution gave a mixture of long needles and hexagonal tablets; this mixture was re-dissolved and diluted, and on cooling tablets alone were obtained. (Found: Br, 30.2; N, 6.7 %; whence Br : N = 1 : 1.27.) On one recrystallisation the plates obtained gave Br, 25.8; N, 7.9 %; whence Br : N = 1 : 1.75, and after a further recrystallisation the pure sesquihydrate crystallising in rectangular tablets, which decompose on heating to 130°, was obtained.

0.1713 g.; 0.0969 g. AgBr. Br = 24.1 %.

0.1904 g.; NH₃ = 11.07 cc. *N*/10 acid. N = 8.1 %.

Calc. for (C₄H₉O₂N)₂.NaBr.1½H₂O; Br = 23.8 %; N = 8.3 %.

For the isolation of the pure 1 : 1 compound indicated by the first analysis, a solution containing two molecules of sodium bromide to one of *N*-dimethylaminoacetic acid was concentrated; after removal of a small amount of sodium bromide, the required compound separated as a monohydrate in hexagonal tablets which decompose slightly on drying at 120°.

0.2108 g.; 0.1780 g. AgBr. Br = 35.9 %.

0.1958 g.; NH₃ = 8.52 cc. *N*/10 acid. N = 6.1 %.

Calc. for C₄H₉O₂N.NaBr.H₂O; Br = 35.7 %; N = 6.3 %.

N-Dimethylaminoacetic acid sodium iodide trihydrate. This compound crystallises in rectangular plates.

0.2095 g.; 0.1582 g. AgI. I = 40.8 %.

0.2063 g.; NH₃ = 6.48 cc. *N*/10 acid. N = 4.4 %.

Calc. for C₄H₉O₂N.NaI.3H₂O; I = 41.3 %; N = 4.6 %.

N-Dimethylaminoacetic acid potassium iodide sesquihydrate. The first crop obtained (rectangular plates) was impure. (Found: I, 38.8; N, 5.4 %; whence I : N = 1 : 1.26); but a second crop of rectangular plates proved to be the pure compound.

0.1894 g.; 0.1504 g. AgI. I = 42.9 %.

0.2070 g.; NH₃ = 7.03 cc. *N*/10 acid. N = 4.8 %.

Calc. for C₄H₉O₂N.KI.1½H₂O; I = 42.9 %; N = 4.7 %.

Attempts to prepare addition compounds of potassium chloride or bromide were unsuccessful, the halide being recovered practically pure in each case.

Addition compounds of N-trimethylaminoacetic acid (betaine).

Penta-betaine di-calcium iodide undecahydrate. On concentration of a solution containing two molecules of betaine to one of calcium iodide, large, glistening, square plates were deposited which were optically isotropic. (Found: N, 5.2; I, 37.0 %; whence N : I = 1 : 0.79.) Recrystallisation gave similar plates. (Found: N, 5.2; I, 37.6 %; whence N : I = 1 : 0.8.)

When an equimolecular solution was concentrated, large, square plates were again obtained—with a similar ratio. (Found: N, 5.1; I, 37.5 %; whence N : I = 1 : 0.8), and on recrystallisation the same compound was obtained.

0.1843 g. dried at 95° lost 0.0169 g. $H_2O = 9.2\%$.

0.1566 g.; 0.1081 g. AgI. $I = 37.3\%$.

0.1835 g.; $NH_3 = 6.91$ cc. $N/10$ acid. $N = 5.3\%$.

0.1843 g.; $C_2O_4Ca = 5.48$ cc. $N/10$ $KMnO_4$. $Ca = 6.0\%$.

Calc. for $(C_5H_{11}O_2N)_5 \cdot (CaI_2)_2 \cdot 11H_2O$; $7H_2O = 9.2\%$; $I = 37.0\%$; $N = 5.1\%$; $Ca = 5.8\%$.

Attempts to prepare compounds of calcium chloride or calcium bromide were unsuccessful, only syrupy solutions being obtained.

Betaine barium iodide tetrahydrate. Concentration of a solution containing two molecules of betaine to one of barium iodide gave woolly needles (0.3 g.) which were impure. (Found: N, 4.8; I, 32.2%; whence $N : I = 1 : 0.75$.) An equimolecular solution deposited a pure compound in rods (5.5 g.).

0.1959 g.; 0.1606 g. AgI. $I = 44.3\%$.

0.2080 g.; $NH_3 = 3.36$ cc. $N/10$ acid. $N = 2.3\%$.

Calc. for $C_5H_{11}O_2N \cdot BaI_2 \cdot 4H_2O$; $I = 43.7\%$; $N = 2.4\%$.

Betaine strontium chloride tetrahydrate. A solution of the components deposited long, silky needles (1.1 g.) on concentration.

0.1931 g. dried at 120° lost 0.0412 g. $H_2O = 21.3\%$.

0.1931 g.; 0.1558 g. AgCl. $Cl = 20.0\%$.

0.2100 g.; $NH_3 = 6.11$ cc. $N/10$ acid. $N = 4.1\%$.

Calc. for $C_5H_{11}O_2N \cdot SrCl_2 \cdot 4H_2O$; $H_2O = 20.7\%$; $Cl = 20.4\%$; $N = 4.0\%$.

Betaine strontium bromide pentahydrate. Concentration of a solution prepared in the usual way gave needles (1.0 g.) which were impure. (Found: N, 4.0; Br, 32.8%; whence $N : Br = 1 : 1.4$.) The mother-liquor on concentration, however, gave a crop of needles (0.3 g.) which were analytically pure.

0.0984 g. dried at 120° lost 0.0199 g. $H_2O = 20.2\%$.

0.0984 g.; 0.0824 g. AgBr. $Br = 35.6\%$.

0.0908 g.; $NH_3 = 1.99$ cc. $N/10$ acid. $N = 3.1\%$.

Calc. for $C_5H_{11}O_2N \cdot SrBr_2 \cdot 5H_2O$; $H_2O = 19.8\%$; $Br = 35.2\%$; $N = 3.1\%$.

Di-betaine strontium iodide tetrahydrate. This compound was obtained in the usual way, crystallising in short needles (0.3 g.).

0.1390 g.; 1015 g. AgI. $I = 39.4\%$.

0.0722 g.; $NH_3 = 1.99$ cc. $N/10$ acid. $N = 3.9\%$.

Calc. for $(C_5H_{11}O_2N)_2 \cdot SrI_2 \cdot 4H_2O$; $I = 39.2\%$; $N = 4.3\%$.

Betaine lithium bromide hydrate. On concentration of the solution, prepared in the usual manner, rods (2.4 g.) were deposited: they were impure. (Found: N, 5.6; Br, 24.6%; whence $N : Br = 1 : 0.77$.) Recrystallisation gave long needles (0.5 g.) which were pure and contained $2\frac{1}{2}$ molecules of water.

0.1910 g. dried at 120° lost 0.0348 g. $H_2O = 18.2\%$.

0.1910 g.; 0.1431 g. AgBr. $Br = 31.9\%$.

0.1918 g.; $NH_3 = 7.52$ cc. $N/10$ acid. $N = 5.5\%$.

Calc. for $C_5H_{11}O_2N \cdot LiBr \cdot 2\frac{1}{2}H_2O$; $H_2O = 18.1\%$; $Br = 32.1\%$; $N = 5.6\%$.

Di-betaine lithium iodide monohydrate. Tufts of needles (1.0 g.) were obtained on concentration of an equimolecular solution.

0.1966 g.; 0.1198 g. AgI. $I = 32.9\%$.

0.2094 g.; $NH_3 = 10.28$ cc. $N/10$ acid. $N = 6.9\%$.

Calc. for $(C_5H_{11}O_2N)_2 \cdot LiI \cdot H_2O$; $I = 32.9\%$; $N = 7.2\%$.

Lithium chloride. When an equimolecular solution of lithium chloride and betaine was concentrated to a syrup, a mixture of needles and small hexagonal

plates was slowly deposited. But when two solutions, one with the components in the ratio 2 : 1 and the other in the ratio 1 : 2, were concentrated, no crystalline substances could be isolated.

Betaine sodium chloride sesquihydrate. On concentration of an equimolecular solution a mixture was obtained. A second solution, however, containing twice the amount of betaine, when concentrated, gave long needles alone.

0.1918 g. dried at 120° lost 0.0294 g. $H_2O = 15.3\%$.

0.1918 g.; 0.1375 g. AgCl. $Cl = 17.7\%$.

0.2040 g.; $NH_3 = 10.23$ cc. *N*/10 acid. $N = 7.0\%$.

Calc. for $C_5H_{11}O_2N \cdot NaCl \cdot 1\frac{1}{2}H_2O$; $H_2O = 13.3\%$; $Cl = 17.5\%$; $N = 6.9\%$.

Di-betaine sodium bromide sesquihydrate. The first crop obtained when an equimolecular solution was concentrated consisted of rods (1.1 g.) which were impure. (Found: N, 4.6; Br, 35.6%; whence $N : Br = 1 : 1.36$.) Concentration of the mother-liquor gave a second crop of glistening, rectangular leaflets (0.3 g.) which analysed correctly.

0.1078 g. dried at 120° lost 0.0093 g. $H_2O = 8.6\%$.

0.1078 g.; 0.0554 g. AgBr. $Br = 21.9\%$.

0.1359 g.; $NH_3 = 7.23$ cc. *N*/10 acid. $N = 7.5\%$.

Calc. for $(C_5H_{11}O_2N)_2 \cdot NaBr \cdot 1\frac{1}{2}H_2O$; $H_2O = 7.4\%$; $Br = 21.9\%$; $N = 7.7\%$.

Betaine sodium iodide trihydrate. Rectangular plates (0.4 g.) were deposited on concentrating an equimolecular solution. They were slightly impure. (Found: N, 3.9; I, 38.1%; whence $N : I = 1 : 1.08$.) The second crop, also rectangular plates, proved to be pure.

0.1985 g.; 0.1449 g. AgI. $I = 39.4\%$.

0.2001 g.; $NH_3 = 5.89$ cc. *N*/10 acid. $N = 4.1\%$.

Calc. for $C_5H_{11}O_2N \cdot NaI \cdot 3H_2O$; $I = 39.2\%$; $N = 4.4\%$.

Betaine ammonium iodide dihydrate. An equimolecular solution deposited rods on concentration. (Found: N, 9.1; I, 45.1%; whence $N : I = 1 : 0.54$.)

The rods were recrystallised, and after removing a small quantity of leaflets, rods were again deposited.

0.2007 g. dried at 120° lost 0.0129 g. $H_2O = 6.4\%$.

0.2007 g.; 0.1575 g. AgI. $I = 42.4\%$.

0.2024 g.; $NH_3 = 13.24$ cc. *N*/10 acid. $N = 9.2\%$.

Calc. for $C_5H_{11}O_2N \cdot NH_4I \cdot 2H_2O$; $H_2O = 6.0\%$; $I = 42.6\%$; $N = 9.4\%$.

From solutions of betaine and ammonium chloride, ammonium bromide and potassium chloride, no addition compounds could be obtained.

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