The N-Methylglucamine Complexes. I. The Lead N-Methylglucamine System

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The lead N-methylglucamine system has been investigated under widely varying conditions of ligand concentration and pH. Polarographic, potentiometric and especially optical rotation measurements have been useful for determining the structures of the several species formed. No complexes are formed at pH values less than 6.5. In the pH range 6.5 to 11.5 four lead dimers containing ol and oxo bridges exist. The successive acidity constants for these species have been estimated by potentiometric and "rotometric" titrations. pK values for the acid ionizations are inserted between formulas: $Pb_2(OH)_2[HNG(OH)_5]_2^{+4}$, 7.7, $Pb_2O(OH)[HNG(OH)_5]_2^{+3}$, 9.4, $Pb_2O_2[HNG(OH)_5]_2^{+2}$, $pK_3 + pK_4 = 20.4$, $Pb_2O_2[NG(OH)_5]_2$, where $HNG(OH)_5^+$ is the N-methylglucammonium ion. At pH 12 several different species may be formed by varying the ratio of lead to N-methylglucamine. A sparingly soluble, very strongly levorotatory 3:1 (lead to N-methylglucamine) compound exists. Evidence is given for a 2:1 soluble species and at least two other species; a 1:4 (or possibly a 1:2) and a 1:1 (or perhaps a 3:2) soluble species. The system has been investigated polarographically in very basic solution ($pH > 13.5$). Only a 1:1 chelate is formed. The most probable structure for this species has been established, and the apparent dissociation constant has been determined for ionic strengths varying from 0.3 to 2.

Recent work of Pecsok and co-workers[1] has shown that extremely stable metal chelates are formed by sodium gluconate in strongly basic solution. N-Methylglucamine, a compound of somewhat similar structure but containing a methylamine function, is now commercially available.[2] This substance has been used to stabilize chlorinated ethylene polymers against metal contaminants[3] and to prepare metal-free phthalocyanines.[4] However, no detailed studies have been made of the metal complexes formed by N-methylglucamine.

It is the purpose of this paper to investigate the structures and, where possible, the stability constants of the various lead N-methylglucamine complexes and to correlate these data with those found for the lead gluconate complexes. Polarographic, potentiometric and polarimetric data were found useful in these investigations.

Experimental

Apparatus and Technique.—Polarograms were taken according to usual technique[5] with a calibrated Sargent Model III Manual Polarograph. The capillary constant, $m^{2/3}t^{1/6}$, was 2.225 mg.$^{2/3}$ sec.$^{-1/2}$ at -1.0 v. vs. S.C.E. Temperatures were maintained at $30.00 \pm 0.02°$. The three-compartment polarographic cell previously described[6] was used since the strongly basic solutions present in several experiments attacked the agar plug in cells of conventional design and eventually would have contaminated the reference electrode. The center compartment of the cell was filled with saturated sodium nitrate solution in most cases.

Optical rotation experiments were carried out with a Franz, Schmidt and Haensch Precision Polarimeter at room temperature ($27 \pm 3°$) using a 4-dm. cell. Each rotation reported is the average of at least seven observations. The average deviation of the readings was less than 0.01°. A light source of 589.3 mμ (Nap light) was used for all measurements. Solutions were allowed to stand at least one week at room temperature before measurements were made to assure equilibrium. For mixtures in which a precipitate was formed, the precipitate was removed by filtration through sintered glass filters before measurements were taken.

(1) (a) R. L. Pecsok and R. S. Juvel, Jr., THIS JOURNAL, **77**, 202 (1955); (b) **78**, 3967 (1956); (c) R. L. Pecsok and J. Sandera, ibil., **77**, 1189 (1955); (d) **79**, 4069 (1957).

(2) E. I. du Pont de Nemours and Co., Inc., Organic Chemicals Dept., Wilmington, Delaware.

(3) A. W. Anderson and S. C. Overbaugh, U. S. Patent 2,511,192 (Feb. 13, 1951); C. A., **45**, 4091 (1951).

(4) F. S. Palmer and P. P. Cross, U. S. Patent 2,113,191 (Dec. 24, 1916); C. A., **41**, 1853 (1947).

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1952.

(6) R. L. Pecsok and R. S. Juvet, Jr., Anal. Chem., **27**, 165 (1955).

All pH measurements were made with a Beckman Model H-2 pH meter. A type E-2 glass electrode was used for pH values greater than 9. Potentiometric titrations were carried out under an atmosphere of nitrogen and in a jacketed cell maintained at 30.0°.

Materials.—Lead solutions were prepared from analytical reagent grade lead nitrate. The solutions were standardized volumetrically by the chromate method[7] or amperometrically with potassium dichromate at zero applied potential.[8]

The N-methylglycamine[2] was recrystallized twice from absolute ethanol, and dried in vacuo. The purified amine was standardized acidimetrically and was found to be 99.7% pure or better.

Anal. Calcd. for $C_7H_{17}NO_5$: C, 43.07; H, 8.78; N, 7.18. Found: C, 43.27; H, 8.71; N, 7.34.

Sodium perchlorate (G. F. Smith Chemical Co.), used to adjust the ionic strength in certain experiments, was shown to be free of chloride, and a 1 M solution was "polarographically pure." All other chemicals were reagent grade.

Polarographic Studies

The conventional log plot[9] was used to establish the reversibility of the polarographic reduction of several lead N-methylglucamine solutions. In a typical case a plot of $E_{d.e.}$ vs. log $i/(i_d - i)$ for 0.5 mM lead in a solution of 0.06 M N-methylglucamine and 1.0 M sodium hydroxide gave a straight line whose slope was -0.0311. This is in good agreement with the theoretical value of -0.0301 for a two electron reduction at 30°.[10] Values of $E_{3/4} - E_{1/4}$ were measured for all polarograms and showed an average value of -0.029 v. in strongly basic N-methylglucamine solutions in exact agreement with the theoretical value of -0.0287 derived for a reversible two electron reduction.[11]

Effect of N-Methylglucamine Concentration in Strongly Basic Solution.—It may be shown[1a] readily that if the concentration of sodium hydroxide is maintained constant and if the concentration of a complexing ligand is varied, a plot of the logarithm of the free uncomplexed ligand concentration vs. the polarographic half-wave potential should give a straight line, the inverse slope of which is $-0.0300S$·

(7) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 229.

(8) I. M. Kolthoff and Y. D. Pan, THIS JOURNAL, **61**, 3402 (1939).

(9) J. J. Lingane, Chem. Revs., **29**, 1 (1941).

(10) Note that at 30.0°, the temperature at which all polarographic data were taken in the present investigation, the value of $RT (\log_e 10)/nF = 0.0301$ v.

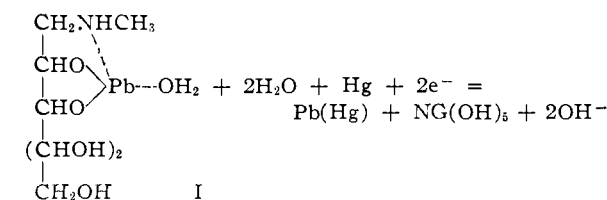(11) I. Tomes, Collection Czechoslov. Chem. Communs., **9**, 12 (1937).

(p), where p is the number of ligand molecules associated with each metal ion.[10]

This effect was studied at concentrations of N-methylglucamine ranging from 0.012 to 0.100 M and various constant concentrations of sodium hydroxide ranging from 0.3 to 2 M. The concentration of lead was 0.5 mM in all cases. The experimental results are plotted in Fig. 1A. A series of straight lines at the various concentrations of sodium hydroxide was obtained with an average inverse slope of −0.027 ± 0.001. This slope corresponds to a value of p = 0.90 ± 0.03 (=1) N-methylglucamine per lead. Therefore at concentrations of sodium hydroxide greater than 0.3 M and in the presence of a large excess of complexing ligand, only a 1:1 lead N-methylglucamine species exists.
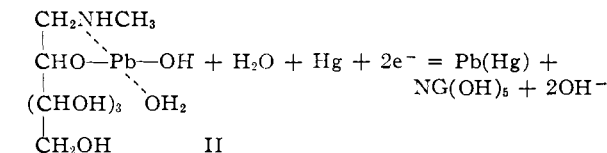
Effect of Hydroxide Concentration.—A study of the effect of changes in hydroxide concentration on the half-wave potential at constant N-methylglucamine concentration is of value in determining the number of secondary hydroxyl groups in the N-methylglucamine molecule associated with the lead in chelate formation.

A plot of log C_{OH^-} vs. $E_{1/2}$ at constant ligand concentration should form a straight line with inverse slope equal to $-0.03008(x)$, where x is the number of hydroxide ions entering into the reduction reaction per lead.[1a,10] In this study sodium hydroxide concentrations varied from 0.24 to 1.20 M at N-methylglucamine concentrations of 0.02, 0.04 and 0.10 M. The ionic strength was adjusted to 2.0 with sodium perchlorate. The experimental results are given in Fig. 1B. Three straight lines were obtained with an inverse slope of −0.059 ± 0.002. This slope corresponds to a value of x equal to 1.96 ± 0.05 (= 2) hydroxides required in the reduction of the lead N-methylglucamine chelate in strongly basic solution.

Apparently the structure of the species present under these conditions and the reduction reaction is either

$$
\begin{array}{c}
\text{CH}_2\text{NHCH}_3 \\
| \quad \backslash \\
\text{CHO} \backslash \\
| \quad \quad \diagup \text{Pb---OH}_2 + 2\text{H}_2\text{O} + \text{Hg} + 2\text{e}^- = \\
\text{CHO} \diagup \quad \quad \quad \quad \text{Pb(Hg)} + \text{NG(OH)}_5 + 2\text{OH}^- \\
| \\
(\text{CHOH})_2 \\
| \\
\text{CH}_2\text{OH} \quad \quad \text{I}
\end{array}
$$

or

$$
\begin{array}{c}
\text{CH}_2\text{NHCH}_3 \\
| \quad \backslash \\
\text{CHO---Pb---OH} + \text{H}_2\text{O} + \text{Hg} + 2\text{e}^- = \text{Pb(Hg)} + \\
| \quad \quad \backslash \quad \quad \quad \quad \quad \quad \quad \text{NG(OH)}_5 + 2\text{OH}^- \\
(\text{CHOH})_3 \quad \text{OH}_2 \\
| \\
\text{CH}_2\text{OH} \quad \quad \text{II}
\end{array}
$$

where N-methylglucamine is symbolized as NG-(OH)₅. Our experimental data will not differentiate between structures I and II.

Equilibrium Constants.—The apparent equilibrium constant for the reaction

$$\text{Complex} + y\text{H}_2\text{O} = \text{Pb}^{++} + \text{NG(OH)}_5 + 2\text{OH}^- \quad (1)$$
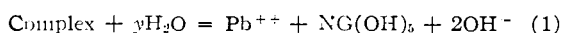
may be determined from polarographic data at various ionic strengths. It has been shown[1a,10] that at 30°
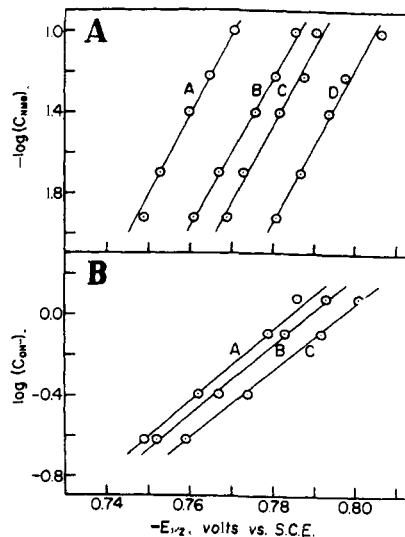

Fig. 1.—Set A, effect of N-methylglucamine concentration on the half-wave potential of lead at various hydroxide ion concentrations: A, 0.300 M; B, 0.650 M; C, 0.991 M; D, 1.981 M NaOH. Set B, effect of hydroxide ion concentration on the half-wave potential of lead at various N-methylglucamine concentrations: A, 0.0200 M; B, 0.0400 M; C, 0.100 M; μ = 2.0.

$$(E_{1/2})_c - (E_{1/2})_s = 0.03008 \log (Kk_s/k_c) -$$
$$0.03008 \log \left(C_{NMG} + p\frac{i_d}{2k_{NMG}} \right)^p (C_{OH^-})^x \quad (2)$$

where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of the complex and simple metal ions, respectively; K is the apparent equilibrium constant of reaction 1; k_s/k_c is equal to the ratio of the square roots of the diffusion coefficients of the simple and complexed metal ions and is also equal to the ratio of the measured diffusion current, i_d, of the simple and complex metal ions when determined for equal concentrations of lead; $pi_d/2k_{NMG}$ is a minor correction term which takes into account the N-methylglucamine produced at the surface of the dropping mercury electrode at the half-wave potential; and p and x are the moles of complexing ligand and hydroxide ion per mole of lead entering into the reduction reaction, respectively.

Rearrangement of equation 2 with proper substitutions leads to the equation

$$pK = \frac{(E_{1/2})_c - (E_{1/2})_s}{-0.03008} - \log \left(C_{NMG} + \right.$$
$$\left. \frac{C_{complex}}{2} \right) (OH^-)^2 + \log \frac{(i_d)_s}{(i_d)_c} \quad (3)$$

Five determinations of the pK value for reaction 1 were made at four different ionic strengths. The results are given in Table I.[12]

Values of $(E_{1/2})_s$ were determined for the polarographic reduction of lead in sodium perchlorate solutions of various concentrations. The $(E_{1/2})_s$ values obtained were: μ = 2.0, −0.372 v.; μ = 1.0, −0.377 v.; μ = 0.65, −0.378 v.; μ = 0.30, −0.379 v. vs. S.C.E. These values are in

(12) In comparison, the pK values for the lead gluconate chelate in strongly basic media range from 10.23 to 15.92 over this same range of ionic strength (ref. 1b).

excellent agreement with those found by Hershenson, Smith and Hume.[13]

Potentiometric Titrations

The titrations of N-methylglucamine and lead nitrate-N-methylglucamine mixtures in the presence of perchloric acid were carried out under nitrogen with carbonate-free sodium hydroxide solutions in a closed vessel thermostated at 30.0°.

Figure 2 shows the potentiometric titration of N-methylglucamine (curve A), a 1:2 lead to N-methylglucamine mixture (curve B), and a 1:1 lead to N-methylglucamine mixture (curve C), each in the presence of excess perchloric acid. The moles of N-methylglucamine and perchloric acid taken were the same for each titration. The abscissa in Fig. 2 has been marked in terms of "a," the moles of hydroxide added per mole of N-methylglucamine present. Values of a less than zero correspond to the titration of the excess perchloric acid.
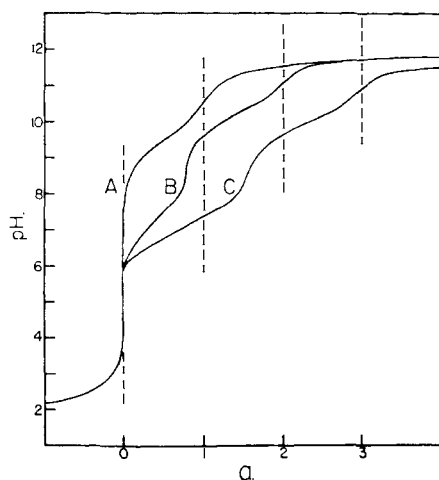

Fig. 2.—Potentiometric titrations: A, N-methylglucamine; B, a 1:2 molar mixture of lead nitrate to N-methylglucamine; C, a 1:1 molar mixture.   Initial concentrations: 14.6 mM N-methylglucamine, 29.8 mM perchloric acid in each case. a is moles of base per mole of ligand.

In curve A the reaction taking place from $a = 0$ to the inflection point at $a = 1$ is the formation of the free amine from the amine perchlorate salt. The pK_b of N-methylglucamine calculated from this curve is 4.35 at 30.0° and $\mu = 0.05$. The negative log of the ion product for water at 30°, $pK_w = 13.83$, was used in calculating this value.[14]

Curve C corresponds to the titration of a 1:1 molar mixture of lead and N-methylglucamine in the presence of excess perchloric acid. Three breaks are apparent in this curve. The first, at $a = 0$, corresponds to the titration of the perchloric acid. The second and third breaks, occurring at exactly $a = 1.5$ and $a = 3.0$, correspond to the base consumed in complex formation. The pH readings in the interval $a = 0.5$ to 1 exhibited a slow drift toward higher pH values. Therefore solutions were allowed to stand 30–45 minutes between readings. Above $a = 1$ equilibrium was estab-

(13) H. M. Hershenson, M. E. Smith and D. N. Hume, This Journal. **75**, 507 (1953).

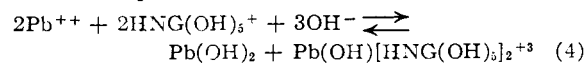(14) II. S. Harned and W. J. Hamer, *ibid.*, **55**, 2194 (1933).

The pK Value of the Lead N-Methylglucamine Chelate in Strongly Basic Media

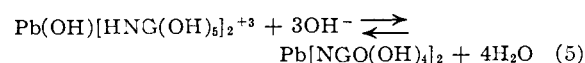| μ	$-(E_{1/2})_c$	C_{OH^-}	C_{NMG}	$\frac{(i_d)_s}{(i_d)_c}$	pK
2.0	0.807	1.981	0.0997	1.48	15.04
2.0	.798	1.981	.0597	1.44	14.96
2.0	.794	1.981	.0397	1.40	14.99
2.0	.787	1.981	.0197	1.35	15.05
2.0	.781	1.981	.0117	1.24	15.03
				Mean	$= 15.01 \pm 0.04$
0.99	0.791	0.991	0.0997	1.44	14.93
.99	.788	.991	.0597	1.42	15.04
.99	.782	.991	.0397	1.38	15.01
.99	.773	.991	.0197	1.35	15.00
.99	.769	.991	.0117	1.32	15.08
				Mean	$= 15.01 \pm 0.06$
0.65	0.786	0.650	0.0997	1.43	15.09
.65	.781	.650	.0597	1.41	15.14
.65	.776	.650	.0397	1.38	15.14
.65	.767	.650	.0197	1.35	15.13
.65	.761	.650	.0117	1.33	15.14
				Mean	$= 15.13 \pm 0.02$
0.30	0.771	0.300	0.0997	1.38	15.21
.30	.765	.300	.0597	1.25	15.20
.30	.760	.300	.0397	1.24	15.21
.30	.753	.300	.0197	1.26	15.28
.30	.749	.300	.0117	1.30	15.39^a
				Mean	$= 15.22 \pm 0.04$

^{a} This value was not included in the average since the polarographic wave was poorly formed at this low concentration of N-methylglucamine and sodium hydroxide.

lished relatively rapidly. In more concentrated solutions (*vide infra*) a precipitate is formed in the pH range 7 to 11.5.
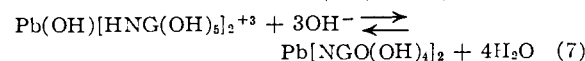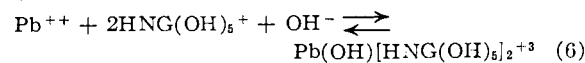
Inflection points occurring at fractional a values have been observed by several workers in the potentiometric titration of metal complexes. These observations may be explained in at least two ways. Courtney, *et al.*,[15] have found for a 1:1 molar mixture of a metal ion and a ligand that in certain instances a 1:2 species is formed accompanied by precipitation of an equimolar amount of metal hydroxide. This can lead to fractional a values. Thus, if the N-methylglucammonium salt is symbolized as $HNG(OH)_5^+$, one must write for the reaction completed at $a = 1.5$

$$2Pb^{++} + 2HNG(OH)_5^+ + 3OH^- \rightleftharpoons$$
$$Pb(OH)_2 + Pb(OH)[HNG(OH)_5]_2^{+3} \quad (4)$$

and then the reaction

$$Pb(OH)[HNG(OH)_5]_2^{+3} + 3OH^- \rightleftharpoons$$
$$Pb[NGO(OH)_4]_2 + 4H_2O \quad (5)$$

complete at $a = 3.0$. However, if these reactions were correct, in the presence of a 1:2 molar mixture (curve B), reactions 6 and 7 should occur

$$Pb^{++} + 2HNG(OH)_5^+ + OH^- \rightleftharpoons$$
$$Pb(OH)[HNG(OH)_5]_2^{+3} \quad (6)$$

$$Pb(OH)[HNG(OH)_5]_2^{+3} + 3OH^- \rightleftharpoons$$
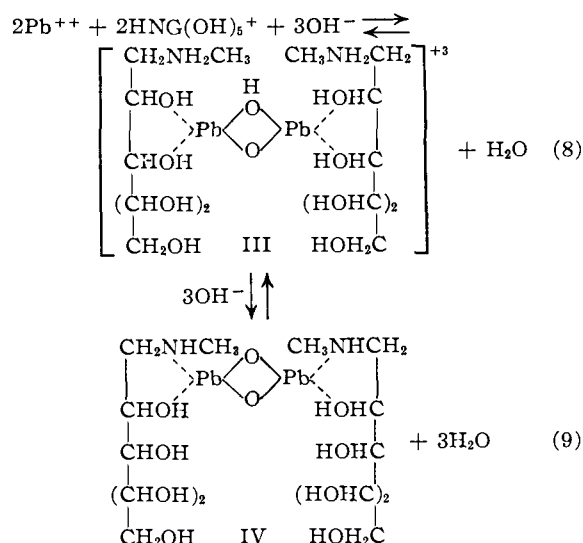$$Pb[NGO(OH)_4]_2 + 4H_2O \quad (7)$$

(15) R. C. Courtney, R. L. Gustafson, S. Chaberek and A. E. Martell, *ibid.*, **80**, 2121 (1958).

Thus, the first inflection point should come at $a = 0.5$ and the second at an a value 1.5 units greater, or $a = 2.0$. The observed inflection points for the 1:2 molar mixture occurred at a values of exactly 0.75 and 2.0. Therefore these reactions clearly are not correct.
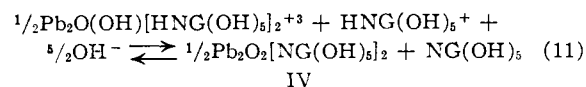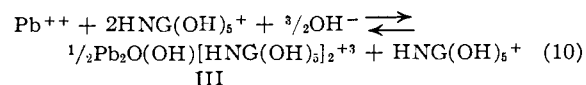
Fractional a values also may be explained by assuming dimerization through ol and oxo bridges.[16] This type structure has been claimed by Pfeiffer[17] and by Werner[18] for compounds as early as 1907. Weinland and Stroh[19] have postulated ol bridges for several basic lead salts on the basis of elemental analysis.

The inflection points obtained for the 1:1 mixture in Fig. 2C may be explained by the reactions

$$2Pb^{++} + 2HNG(OH)_5^+ + 3OH^- \rightleftharpoons$$

$$\begin{bmatrix} CH_2NH_2CH_3 & CH_3NH_2CH_2 \\ CHOH & \underset{O}{\overset{H}{\diamond}} & HOHC \\ \diamond Pb \diamond & \diamond Pb \diamond \\ CHOH & O & HOHC \\ (CHOH)_2 & (HOHC)_2 \\ CH_2OH & III & HOH_2C \end{bmatrix}^{+3} + H_2O \quad (8)$$

$$3OH^- \downarrow\uparrow$$

$$\begin{array}{cc} CH_2NHCH_3 & CH_3NHCH_2 \\ \diamond Pb \diamond & \diamond Pb \diamond \\ CHOH & O & HOHC \\ CHOH & HOHC \\ (CHOH)_2 & (HOHC)_2 \\ CH_2OH & IV & HOH_2C \end{array} + 3H_2O \quad (9)$$

If these reactions are correct, compound III is formed in the pH range 6–8.5. A pH less than 8.5 is not sufficiently basic to neutralize the protonated amine (cf. curve A). In the pH range 8.5–11 compound IV apparently is formed by neutralization of the amine salt and oxolation of the ol bridge. These reactions lead to inflection points at a values of 1.5 and 3.0, in agreement with experimental results.

For the 1:2 mixture (curve B) inflection points at a values of 0.75 and 2.0 would be expected in accordance with reactions 10 and 11.

$$Pb^{++} + 2HNG(OH)_5^+ + {}^3/_2OH^- \rightleftharpoons$$
$$^1/_2Pb_2O(OH)[HNG(OH)_5]_2^{+3} + HNG(OH)_5^+ \quad (10)$$
$$III$$

$$^1/_2Pb_2O(OH)[HNG(OH)_5]_2^{+3} + HNG(OH)_5^+ +$$
$$^5/_2OH^- \rightleftharpoons {}^1/_2Pb_2O_2[NG(OH)_5]_2 + NG(OH)_5 \quad (11)$$
$$IV$$

This is also in agreement with all experimental results. The structures and the pH ranges at which transitions take place seem reasonable in the light of present knowledge of olation. Optical rotation studies discussed below give considerable added weight to these arguments. It is not likely

(16) J. C. Bailar, Jr., ed., "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, pp. 448–471.
(17) P. Pfeiffer, Z. anorg. Chem., 56, 261 (1907).
(18) A. Werner, Ber., 40, 4437 (1907).
(19) R. Weinland and R. Stroh, ibid., 55, 2706 (1922).

that the hydrogens on the secondary hydroxyl groups are neutralized at pH values less than 11.

Optical Rotation Measurements

A plot of observed optical rotation (maintaining the total concentration of the optically active ligand constant throughout the plot) as a function of the pH has been termed a "Rotometric Titration" by Pecsok and Juvet.[1b,20] Such a plot is of value in determining the pH range in which optically active metal chelates exist.

Curve A of Fig. 3 is the rotometric titration of free N-methylglucamine and curve B is that of a
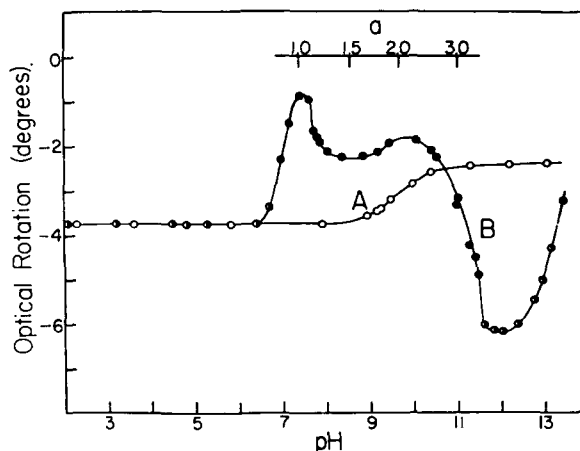

Fig. 3.—"Rotometric" titrations: concentration of total N-methylglucamine species = 0.200 F in each case: A, ⊙, N-methylglucamine in the absence of lead; B, 1:1 molar mixture of lead nitrate and N-methylglucamine, ◐ soluble, ● precipitate formed. a is moles of base per mole of ligand (marked for curve B only).

1:1 molar mixture of lead nitrate and N-methylglucamine. The total concentration of the N-methylglucamine species (the amine, the amine salt and the various complexes) in all cases was 0.2 M except in those instances in which a precipitate was formed. In such cases the precipitate was removed by filtration before rotation readings were taken. Carbonate-free sodium hydroxide or perchloric acid was used to adjust the pH.

In curve A the optical rotation at pH values less than ca. 8 ($-3.748°$) corresponds to that of the amine perchlorate salt. Optical rotation at pH values greater than ca. 12 ($-2.370°$) corresponds to that of the free amine. This difference in optical rotation may be attributed to differences in solvation, and hence in the effective size of the group, between the charged amine salt and the neutral amine.[21] The difference in optical rotation becomes greater at shorter wave lengths of incident polarized light. In the region pH 9 to 10 both the amine salt and the free amine exist. These optical rotation measurements may be used to determine

(20) In this and in the former publication (ref. 1b) this name is a misnomer since each point corresponds to the rotation of an individually prepared solution, and a titration, in the usual sense of the word, was not performed. Presumably, however, apparatus could be designed so that experiments of this nature could be carried out conveniently by titration for cases in which equilibrium is established rapidly. Experiments along this line are being studied and will be reported elsewhere.
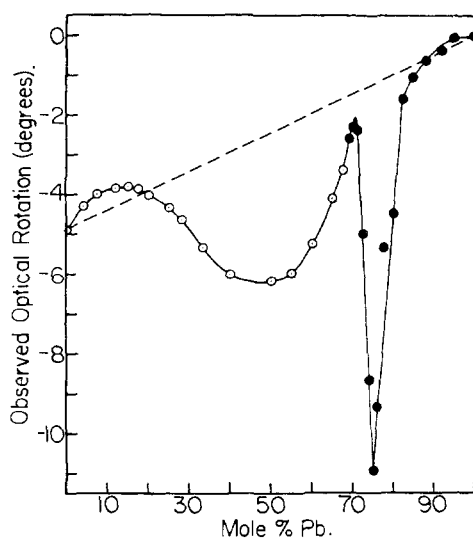(21) R. E. Reeves and F. A. Blouin, THIS JOURNAL, 79, 2261 (1957).

Fig. 4.—Rotometric continuous variation at pH 12.0 $\pm$ 0.2; $(Pb)_{total}$ + $[NG(OH)_5]_{total}$ = 0.400 M for each point: O, soluble; ●, precipitate formed. Dashed line is rotation due to free ligand if no complexation had occurred.

the pK_b of the N-methylglucamine. It is easily shown that the free amine and the amine salt should both be 0.1 M when the optical rotation equals $-3.059°$. The pH reading at this optical rotation is 9.62 which corresponds to a pK_b of 4.23 at 28° and μ = 0.1. The value pK_w = 13.85 at 28° was used in calculating this value.[14] This value for pK_b may be compared with the value 4.35 obtained potentiometrically at 30.0° and μ = 0.05.

A 1:1 molar mixture of lead nitrate and N-methylglucamine (curve B) exhibits an optical rotation identical to that of an equal concentration of the free ligand at pH values less than ca. 6.5. Evidently no complexation occurs in this pH region. This is in agreement with polarographic evidence.

A precipitate is formed in the region pH 7 to 11.5 with an accompanying shift in rotation. Maxima occur at pH 7.4 and 9.7. A minimum occurs at pH 8.5. It is of interest to compare this rotometric titration with the potentiometric titration of the 1:1 mixture (Fig. 2C). It will be noted that the first maximum corresponds almost exactly with the pH at a = 1; the minimum, at a = 1.5; and the second maximum, at a = 2. No sharp change in slope occurs at a = 3. Maxima or minima in a rotometric titration have previously[1b] been interpreted as occurring at that pH at which an optically active complex is present at maximum concentration. These data show the presence of stable compounds at a values of 1, 1.5 and 2. The proposed structure for the compound at a = 1.5 contains an ol and oxo bridge (compound III). A structure for the compound present at pH 7.4 (a = 1) which is consistent with all previous data contains a diol bridge, shown as V. The formation of compound V would explain the slow equilibrium observed in the potentiometric titration at a values less than 1 for the 1:1 mixture and less than 0.5 for the 1:2 mixture. At higher a values, in which simple neutralization of ol

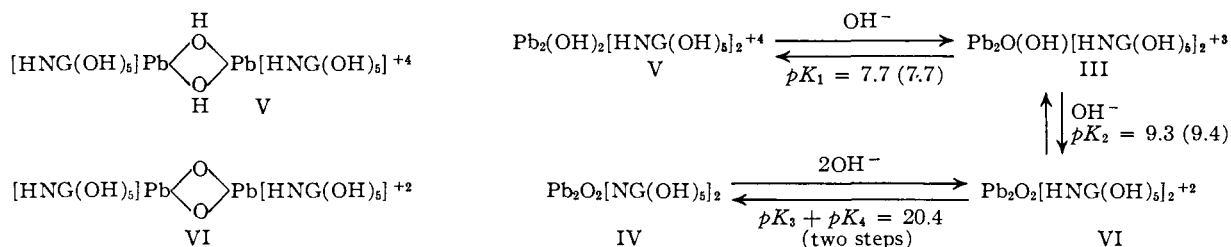bridges takes place, equilibrium is established much more rapidly.

A structure for the compound present at pH 9.7 (a = 2), consistent with all previous data, contains a dioxo bridge. Compounds III, V and VI are likely present as the sparingly soluble nitrate salts. It should be pointed out that compounds V and VI were not detected in the potentiometric titrations. Perhaps this was due to the difference in time allowed for equilibration, to differences in concentrations or to similarities in acidity constants of successive complexes. Compound IV was not detected by the rotometric titration since apparently the optical activity of this compound, under these conditions, is between that of compound VI and those species present at pH 12. The two techniques are complementary.

An estimate of successive acid dissociation constants may be made from the potentiometric and rotometric titrations. The inflection points in the rotometric titration represent the pH values at which there is the greatest rate of change in the concentration of the rotating species with pH, $i.e.$, the pK value for the acid dissociation of the species involved. Likewise, an estimate of the acid dissociation constants may be made from measured pH values at a = 1.25, 1.75 and 2.5. The following values are obtained (values from the rotometric titration in parentheses).

Above pH 11.5 the precipitate redissolves and the rotation shows a minimum at about pH 12. At still greater pH values the optical rotation becomes less negative and approaches that of the complex present in the very basic region, which was studied polarographically.

"Rotometric" Continuous Variations.—Figure 4 is a "rotometric" continuous variations plot at pH 12.0 $\pm$ 0.2. The observed optical rotation is plotted against the mole % lead. The sum of the concentrations of lead nitrate plus N-methylglucamine is 0.400 M for each point. The dashed line is the optical rotation of N-methylglucamine which would have been observed if no complexation had occurred.

Care must be used in the interpretation of this curve since apparently several lead N-methylglucamine species can exist at this pH, and each influences the over-all optical activity of the solution. A maximum and minimum occur at ca. 15 and 50 mole % lead, respectively. One may only conclude that in the presence of a large excess of the ligand, a metal complex exists which has an optical activity less negative than that of the free ligand. However, as the proportion of lead is increased above 15 mole %, a relatively strong levorotatory species is formed to an extent large enough to shift the observed rotation to more negative values. The relatively positive rotating species may be a 1:4 species (20 mole % Pb) or even a 1:2 species (33.3 mole % Pb). The relatively strong levorotatory species is most likely either a 1:1 species (50 mole %) or a 3:2 soluble complex (60 mole %). Conclusive identification of these species cannot be made from our data. It should be mentioned that only a 3:2 soluble complex exists at pH 11.5 for the lead gluconate sys-

$$[HNG(OH)_5]Pb \overset{\overset{H}{O}}{\underset{\overset{O}{H}}{<\ >}} Pb[HNG(OH)_5]^{+4}$$
V

$$Pb_2(OH)_2[HNG(OH)_5]_2^{+4} \underset{pK_1 = 7.7 (7.7)}{\overset{OH^-}{\rightleftharpoons}} Pb_2O(OH)[HNG(OH)_5]_2^{+3}$$
V   III

$$\updownarrow \begin{matrix} OH^- \\ pK_2 = 9.3 (9.4) \end{matrix}$$

$$[HNG(OH)_5]Pb \overset{O}{\underset{O}{<\ >}} Pb[HNG(OH)_5]^{+2}$$
VI

$$Pb_2O_2[NG(OH)_5]_2 \underset{\substack{pK_3 + pK_4 = 20.4 \\ (two\ steps)}}{\overset{2OH^-}{\rightleftharpoons}} Pb_2O_2[HNG(OH)_5]_2^{+2}$$
IV   VI

tem.[1b] Above 50 mole % lead the optical rotation again becomes more positive, and a precipitate forms for mixtures in excess of 67 mole % lead. These data can only be explained by the presence of a relatively positive-rotating, soluble 2:1 complex (66.7 mole % Pb). It is interesting to note that above 70 mole % lead the optical activity becomes strongly negative even though an appreciable amount of the mixture has precipitated. A sharp minimum occurs at 75 mole % lead. These results can only be explained by concluding that the precipitate formed is a partially soluble, strongly levo-rotatory 3:1 solid. Apparently this compound has a large enough solubility to strongly influence the optical activity of the solution.

Preparation and Analysis of the 3:1 Lead N-Methylglu-camine Solid.—A mixture of 0.9761 g. (0.005 mole) of N-methylglucamine and 37.50 ml. of 0.4000 M (0.015 mole) lead nitrate solution was adjusted to pH 12.0 with sodium hydroxide. The mixture was made to volume in a 50-ml. volumetric flask, immersed in a steam-bath for 4 hr. and allowed to stand overnight at room temperature. The white precipitate was filtered under an atmosphere of nitrogen, washed rapidly four times with boiled distilled water and twice with ethanol, and dried *in vacuo* (0.01 μ) for 4.5 hr.

Anal. Calcd. for $Pb_3C_7H_{13}NO_6$: C, 10.15; H, 1.58; N, 1.69; Pb, 75.1. Found: C, 10.21; H, 1.72; N, 2.42; Pb, 73.4 (polarographically).

The high results for nitrogen might be explained by inadequate removal of nitrate nitrogen by this washing technique. No suitable solvent could be found for recrystallization. The analysis is sufficiently consistent with the calculated values to confirm that a 3:1 solid was formed.

URBANA, ILLINOIS

Radiolysis of Neutral Water by Cyclotron Produced Deuterons and Helium Ions[1]

BY HAROLD A. SCHWARZ, JAMES M. CAFFREY, JR., AND GEORGE SCHOLES

The yields of H_2, H_2O_2, H and OH in neutral aqueous solutions have been determined for 18 Mev. deuterons, 32 Mev. helium ions and 11 Mev. helium ions. H_2 yields were determined in KBr and KNO_2 solutions, H_2O_2 yields in air-saturated KBr solutions and H atom yields in solutions of H_2 and O_2 and in solutions of C_2H_5OH and O_2. The dependence of these yields on solute concentration was studied. The results are interpreted in terms of the radical-diffusion mechanism and are found to be in good agreement with the predictions of Ganguly and Magee, based on a simple model of this mechanism except in the densest tracks, where the yield of water decomposition appears to increase. The mechanism whereby radiation decomposes water into free radicals is discussed in the light of the existing data.

Water is decomposed into four products, H_2, H_2O_2, H and OH, by ionizing radiation.[2] The ratio of the molecular products, H_2 and H_2O_2, to the radical products is greater for radiations with a high rate of energy loss, $-dE/dx$, than for radiations of low $-dE/dx$.

The H_2 and H_2O_2 are generally postulated to be formed by combination reactions of the two radicals H and OH in the regions of high radical concentration along the track of the radiation.

$$H + H \longrightarrow H_2 \qquad (1)$$
$$OH + OH \longrightarrow H_2O_2 \qquad (2)$$
$$H + OH \longrightarrow H_2O \qquad (3)$$
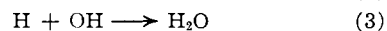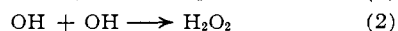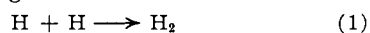
The last reaction has not been observed, but is inferred from the other two. Radicals that do not combine react with solutes present, giving rise to the "radical yields." In the case of γ-rays and fast electrons, these radicals are produced in isolated spurs of a radius of about 10 Å. containing 5 to 10 radicals[3] (*i.e.*, about 100 e.v. of absorbed energy). For particles of higher $-dE/dx$, the spurs may overlap. For a 1 Mev. electron, $-dE/dx$ is 0.02 e.v./Å.[4]; for an 18 Mev. deuteron, 0.5 e.v./Å.; for a 32 Mev. helium ion, 2.3 e.v./Å. and for a 3.5 Mev. α-particle, about 10 e.v./Å. Thus at high $-dE/dx$, the spur structure is lost and the track consists of a concentrated column of radicals.

This mechanism accounts qualitatively for the variation of the product yields with $-dE/dx$ and for the decrease in molecular yields upon the addition of solutes reactive to H and OH.[5,6]

The yields of the molecular and radical products in 0.4 M H_2SO_4 for various cyclotron radiations have been determined by Schuler and Allen,[4]

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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(6) H. A. Schwarz, *ibid.*, 77, 4960 (1955).