This formulation for the structure would explain the lack of an observable double bond absorption band in the infrared region. The chloride groups in such a molecule would be very labile, due to the *trans*-platinum–olefin bond, and this explains the ease of formation of the di-iodo derivative. The observed molecular weights and dipole moments are of the expected order of magnitudes for such a configuration. The inability to form a di-alkoxy derivative is apparently due to the size of such groups. It has been found that a mono-methoxy or mono-ethoxy derivative can be formed readily; however, it has not been possible to isolate a mono-propoxy derivative or any dialkoxy derivatives.

The ability of certain diolefins to chelate with platinum seems to depend on the distance between the double bonds and the ability of the molecule to assume a configuration in which the axes of the double bonds are in the same plane and approximately parallel to each other.

Acknowledgment.—We gratefully acknowledge the assistance of Mr. Jack Baudean of Perkin–Elmer Corporation in New Orleans and Mr. R. T. O'Connor of the Southern Regional Research Laboratory in New Orleans for determining the infrared spectra.

NEW ORLEANS 18, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES, AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

The Gluconate Complexes. III. The Lead Gluconate System[1]

BY ROBERT L. PECSOK AND RICHARD S. JUVET, JR.

RECEIVED FEBRUARY 20, 1956

The lead gluconate system has been investigated under widely varying conditions of basic strength and gluconate concentration. A technique involving optical rotation measurements has supplied useful information for determining the structures of the species present in the *p*H range 1 to 12. A 1:1 species, $PbGH_4^+$, present in the *p*H range 1 to 6, is at maximum concentration at *p*H 3 7. The *pK* for this species is 2.6 ± 0.1 (determined polarographically). In the *p*H range 6 to 10 a solid or mixture of solid lead gluconate complexes is formed. In the *p*H range 10.5 to 12.5 a levorotatory, negatively charged, 3:2 lead gluconate species exists which reaches maximum concentration at *p*H 11.5. In the presence of excess lead a 3:1 lead gluconate solid also forms at this *p*H. In strongly basic media the predominant species is a 1:1 chelate. The dissociation constant of this species has been determined polarographically for ionic strengths varying from 3 to 0.1.

Preliminary experiments with the gluconate chelates of a large number of transition metals indicated the excellent chelating ability of gluconic acid in strongly basic media. The present study is a continuation of the investigation of the structures and stabilities of the various species present under widely varying conditions of basic strength and gluconate concentration. The procedures used are, in general, similar to those described in the previous papers of this series on the glucono-copper[2a] and the glucono-ferric iron systems.[2b] A method involving optical rotation measurements has been useful in determining the structures of the species present in the *p*H range 1 to 12.

Pepinsky[3] has measured the space group and lead positions in the simple salt, lead gluconate, $Pb(C_6H_{11}O_7)_2$, by X-ray measurements, but no attempt has been made to determine the structures of the species which exist in solution. Schmidt[4] has reviewed the history of the use of lead in cancer studies. A number of complex lead salts for use in animal tumor experiments were prepared, among which was calcium lead gluconate (*ca.* 17% Pb). However, the solid reported may have been a mixture of compounds since the percentage of lead is far smaller than would be expected for any likely compound. No previous study has been reported for the various lead gluconate species present in solution.

Experimental

Apparatus and Technique.—Polarograms were recorded according to usual technique[5] with a calibrated Sargent Model XXI Recording Polarograph. Corrections for *IR* drop through the cell were made where necessary, and corrections were made for residual currents in determining all diffusion current data. The rate of flow, *m*, was 1.452 mg. sec.$^{-1}$, and the drop time was 5.41 sec. at −1.0 v. *vs.* S.C.E. at which most measurements of the diffusion current were made. Temperatures were maintained at 25.0°. 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 would eventually have contaminated the reference electrode.

Optical rotation experiments were carried out with a Hilger Standard Polarimeter at room temperature (25 ± 2°) using a 4-dm. cell. Each rotation reported is the average of at least eight observations. The average deviation of the readings is ±0.01°. A sodium vapor lamp was used for all measurements. For solutions in which a precipitate was formed, the precipitate was removed by centrifugation before measurements were made.

All *p*H measurements were made with a Beckman Model H-2 *p*H meter. A type-E glass electrode was used for *p*H values greater than 10. Special precautions were necessary when measuring *p*H values in concentrated perchlorate solutions to prevent apparent drift in *p*H caused by precipitation of potassium perchlorate at the tip of the calomel electrode. A saturated sodium chloride calomel reference electrode (made simply by exchanging the saturated potassium chloride in a Beckman calomel electrode with sodium chloride saturated with mercurous chloride) was used for measuring *p*H in solutions containing large concentrations

(1) Taken in part from a thesis submitted by R. S. Juvet, Jr., to the faculty of the University of California, Los Angeles, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) R. L. Pecsok and R. S. Juvet, Jr., THIS JOURNAL, **77**, 202 (1955); (b) R. L. Pecsok and J. Sandera, *ibid.*, **77**, 1489 (1955).

(3) R. Pepinsky, *Phys. Rev.*, **61**, 726 (1942).

(4) H. Schmidt, *Med. u. Chem. Abhandl. med.-chem. Forschungsstätten I. G. Farbenind.*, **3**, 418 (1936); *C.A.* **31**, 5861 (1937).

(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).

of perchlorate ion. Comparison with standard buffers indicated readings checked within 0.03 *p*H unit over the *p*H range 4 to 9.

Migration experiments were carried out in an 8 mm. o.d. U-tube containing a stopcock in each arm. The center compartment was filled with a solution containing lead and a fivefold excess of gluconate at the desired *p*H. Approximately 25 ml. of solution was required. The stopcocks were then closed and the upper arms were filled to the same height with a gluconate solution of the same concentration and *p*H. Platinum electrodes were inserted, the stopcocks were carefully opened and a potential of 10 v. was applied overnight. Migration was determined by polarographic analysis for lead in the arms of the U-tube.

Materials.—Lead solutions were prepared either from recrystallized reagent grade lead nitrate dried 4 hr. at 130° or from lead perchlorate prepared according to Hershenson, *et al.*[7] The solutions were standardized amperometrically with potassium dichromate at zero applied potential according to the method of Kolthoff and Pan.[8]

Sodium gluconate solutions (Symbolized as $NaGH_4$ with H's referring to secondary hydroxyl hydrogens) were prepared and standardized as previously described.[2a] A 1 *M* solution of sodium perchlorate (G. F. Smith Chemical Co.) was shown to be free of chloride and polarographically pure. All other chemicals were reagent grade.

Discussion and Results

"Rotometric" Titrations.—A study of optical rotation as a function of *p*H and solution composition has been helpful in determining the species present in solution under different conditions.[9] If the optical rotations of various mole ratios of lead to gluconate are plotted (keeping the total concentration of the gluconate constant in all cases) as a function of *p*H, curves are obtained as shown in Fig. 1. The name "Rotometric Titration" is suggested to describe this technique.[9] The total concentration of the gluconate species (the acid, the salt, the complex and the δ- and γ-lactones) in all cases was 0.2 *M*. The ionic strength was adjusted to 2.1 with sodium perchlorate. Runs were made for ratios of lead to gluconate of 2:3, 1:1 and 3:2. The solutions were allowed to stand 2 days at room temperature before measurements were made in an attempt to assure equilibrium. Two minima were found in each case—one at approximately *p*H 3.7 and the other at about *p*H 11.5. No measurements in the *p*H range 6 to 10.5 were made since precipitation interfered. A rotometric titration of 0.2 *M* glucono-δ-lactone in the absence of lead was also run. Poorly reproducible points were obtained below *ca.* *p*H 3 for these solutions probably because of a non-equilibrium mixture of the various species present. In the presence of lead, optical rotation readings are much more reproducible.

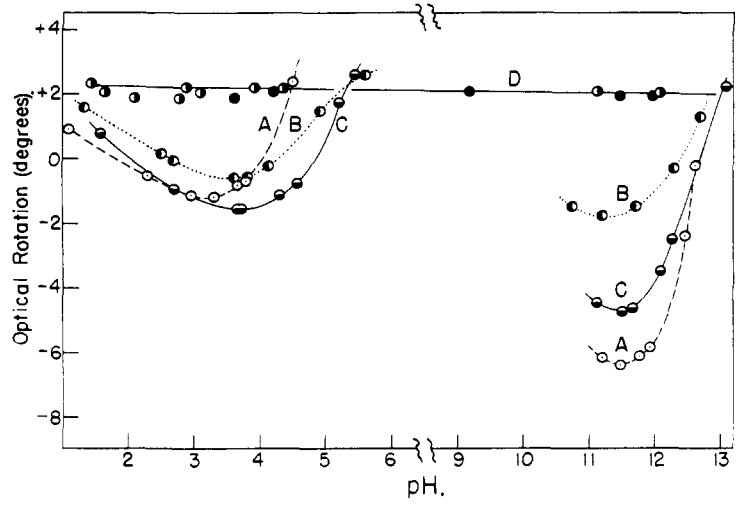


Fig. 1.—"Rotometric titrations" of lead gluconate complexes; concentration of total gluconate species = 0.200 *M* in each case, μ = 2.1. Molar ratio of lead to gluconate: A ○, 3:2; B ◐, 2:3; C ◒, 1:1; and D ◑, sodium gluconate in absence of lead; ● indicates lead gluconate (1:1) in presence of 0.2 *M* EDTA.

Since the rotation of the lead gluconate mixtures begins to deviate from that of free gluconate at *p*H values as low as 1, it seems reasonable to conclude that a lead gluconate complex is formed even at that low *p*H. As the *p*H is increased, the rotation becomes more negative until the *p*H is about 3.7. This indicates that some negative rotating species is produced and that it reaches maximum concentration near *p*H 3.7. Further increase of the *p*H produces rotations with more positive values. Rotations as much as 0.5° more positive than that of free gluconate were obtained before precipitation occurred. Therefore the positive shift in rotation must be caused by the formation of a dextrorotatory lead gluconate species.

Above about *p*H 10.5 the precipitate redissolves, and the rotation shows another minimum at about *p*H 11.5. At greater *p*H values the rotation again becomes more positive. Apparently the complex present in this basic *p*H range is at maximum concentration at *p*H 11.5. The fact that at *p*H 11.5 the rotometric titration curve of the 3:2 mixture is more negative than that of the 1:1 mixture can be explained only if the complex present at this *p*H has a ratio of lead to gluconate greater than 1:1. This interpretation is shown to be correct by a method of "rotometric" continuous variations described below.

In some experiments the solutions were made 0.2 *M* in sodium ethylenediaminetetraacetate (EDTA) in addition to 0.2 *M* in lead gluconate (1:1). The optical rotation was found to be only slightly less than that of free sodium gluconate solutions. Since lead-EDTA is optically inactive, we interpret this to show that the lead-EDTA complex is more stable than the lead gluconate complex at the *p*H values studied and that most of the lead is tied up as lead-EDTA, thus liberating free gluconate ion.

"Rotometric" Continuous Variations.—The method of "rotometric" continuous variations is similar to the spectrophotometric continuous variations method of Job.[10] Figure 2 is the roto-

(7) H. M. Hershenson, M. E. Smith and D. N. Hume, THIS JOURNAL, **75**, 507 (1953).

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

(9) Actually this name is a misnomer for the present investigations 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.

(10) P. Job, *Ann. Chem.*, [10] **9**, 113 (1928); see also W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

metric continuous variation curve for lead gluconate at (A) *p*H 11.5 ± 0.2 and (B) *p*H 3.7 ± 0.2, the *p*H values corresponding to the maximum concentrations of the two species. The sum of the concentrations of lead nitrate plus sodium gluconate is 0.400 *M* for each point. The observed optical rotation is plotted against mole % lead. At *p*H 11.5 two breaks were found—one at *ca.* 60 mole % lead and another at *ca.* 75 mole % lead. Sixty mole % corresponds to a 3:2 lead gluconate complex and 75 mole % corresponds to a 3:1 lead gluconate complex. At mole percentages of lead much greater than 60%, a precipitate forms which was removed by centrifugation prior to determination of optical rotation. At mole percentages of lead greater than 75%, the optical rotation is very close to zero, a result suggesting that all the gluconate is precipitated. These data show that at *p*H 11.5 the species in solution contains three lead atoms and two gluconate molecules. The precipitate formed by addition of excess lead contains three lead atoms per gluconate molecule.

Curve B of Fig. 2 is the rotometric continuous variation curve for lead gluconate at *p*H 3.7 ± 0.2. Difficulty was encountered in preparing the solutions for this curve, especially those solutions with less than 50 mole % lead. Each solution required two to three days to reach equilibrium, and the *p*H was continually changing, a condition requiring addition of base from time-to-time in order to maintain the desired *p*H. After two days, the drop in *p*H was too small to be detected over a period of an hour, and it was assumed that equilibrium had been attained. The solutions were made to volume with a small amount of distilled water and allowed to stand an additional day before rotations were measured. The *p*H was rechecked after rotation measurements. Non-linearity of the curve below 50 mole % might be caused by either a non-equilibrium condition or the presence of some other species with a mole ratio of lead to gluconate less than 1:1. Polarographic evidence does not support the latter conclusion. The fact that the minimum in the curve occurs at 50 mole % lead indicates the presence of a 1:1 complex. This is confirmed by polarographic evidence given below.

Migration Studies.—The center compartment of the migration cell was filled with a solution containing 0.04 *M* lead nitrate and 0.2 *M* sodium gluconate at *p*H 3.7. Both arms of the cell were filled with 0.2 *M* sodium gluconate at *p*H 3.7. Electrolysis was carried out at 10 volts with a Sargent–Slomin Electrolytic Analyzer. Hydrogen was not noticeably evolved. After 18 hr. of electrolysis, a small red coating (presumably PbO_2) was present on the anode and a dull coating (presumably Pb) was present on the cathode. After electrolysis the stopcocks were closed, and the deposits slowly dissolved off both the anode and the cathode.[11] The final *p*H of the anolyte was 2.8, of the catholyte, 3.6. Polarographic analysis of the solutions showed that the catholyte contained 13.2 times more lead than the anolyte. Therefore the species present at *p*H 3.7 is positively charged.

(11) Independent experiments have shown that both a freshly sanded piece of lead and lead dioxide dissolve slightly in sodium gluconate solution.

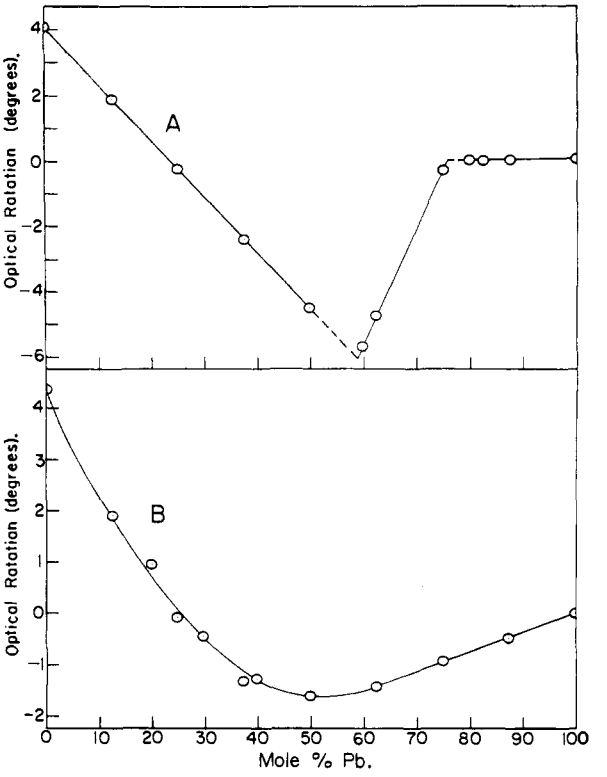


Fig. 2.—Rotometric continuous variations at constant *p*H: $(Pb)_{total} + (NaGH_4)_{total} = 0.400$ *M* for each point: A, *p*H 11.5 ± 0.2; B, *p*H 3.7 ± 0.2.

This same experiment was repeated at *p*H 11.5. At this *p*H the anolyte contained 184 times more lead than the catholyte after 24 hours of electrolysis. This proves that the 3:2 lead complex present at *p*H 11.5 is negatively charged.

Polarographic Studies

Reversibility of the polarographic waves was checked by comparing the half-wave potential of lead in 0.08 *M* sodium gluconate and 1.2 *M* sodium hydroxide with that of lead amalgam (prepared electrolytically) in the same concentration of gluconate and hydroxide. After correction for *IR* drop through the cell, the cathodic and anodic waves had half-wave potentials which checked within 2 mv. Values of $E_{3/4} - E_{1/4}$ were measured for all polarograms and showed an average value of −0.028 v. in strongly basic gluconate solutions in exact agreement with the theoretical value derived by Tomes[12] for a reversible two electron reduction. The values of $E_{3/4} - E_{1/4}$ in more acidic solution (*p*H 2 to 5) averaged −0.033 v. in fair agreement with theory, but indicating a slight degree of irreversibility. At *p*H values 6 to 11 only irreversible polarographic waves with large maxima were observed.

Effect of Gluconate Concentration in Acidic Solution.—In the *p*H range 2 to 5 well-formed, practically reversible polarographic waves are obtained. The effect of the concentration of gluconate on the half-wave potential of lead at *p*H 3.8 ± 0.1 has been investigated. The solutions contained 1 m*M* lead perchlorate, and the center

(12) J. Tomes, *Collection Czechoslav. Chem. Communs.*, **9**, 12, 81, 150 (1937).

compartment of the polarographic cell[6] was filled with a potassium nitrate solution to prevent any diffusion of chloride ions into the solution under investigation. Sodium perchlorate was used to adjust the ionic strength to 0.1 M except in the case of a few solutions in which the ionic strength was already greater than 0.1. The solutions were allowed to stand 3 hr. before polarograms were run to assure equilibrium, which is slowly attained at this pH. If pH is maintained constant at 3.8, a plot of log $(C_{GH_4^-})$ total *vs.* $(E_{1/2})_c$ should from a straight line whose slope is $0.0296(p)$, where p is the number of gluconate molecules associated per lead.[2a] The experimental points did follow a linear relationship and the slope of the best straight line through the points was 0.0314, which corresponds to a value of p equal to 1.06 gluconates per lead. Therefore the species present at this pH is a 1:1 complex. This is in agreement with the rotation studies.

Effect of pH.—The effect of pH on the half-wave potential of lead gluconate was investigated. Figure 3A, a plot of $(E_{1/2})_c$ *vs.* pH in the pH range 2 to 5.5, is an exponential curve instead of a linear curve, as might at first be expected. In such a system, two effects are being measured: (1) the effect of hydrogen ion concentration on the half-wave potential and (2) the effect of the increase

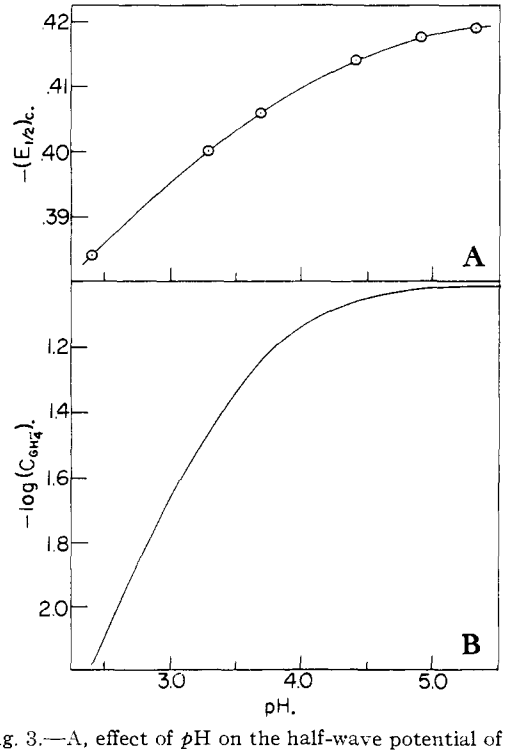


Fig. 3.—A, effect of pH on the half-wave potential of lead gluconate in acidic solution, total gluconate = 0.100 M; B, effect of pH on the concentration of free gluconate ion (calculated from eq. 3).

in free gluconate ion concentration as the pH is increased by neutralization of the gluconic acid and of the γ- and δ-lactones. An expression may be derived for calculating the concentration of free gluconate ion and a correction may be made in order that the dependence of $(E_{1/2})_c$ on hydrogen ion concentration alone may be determined.

If we assume the presence of only a 1:1 lead gluconate species in solution in this pH range, the total concentration of gluconic acid species present, $(G)_t$, is equal to the sum of the concentrations of free acid, the gluconate ion, the lead complex and the two lactones, where $(PbGH_{(4-x)})$ is the concentration of the complex involving an unknown number of secondary hydroxyl groups.

$$(G)_t = (HGH_4) + (GH_4^-) + (PbGH_{(4-x)}) + (\delta\text{-GL}) + (\gamma\text{-GL}) \quad (1)$$

Cannon and Kibrick[13] have reported the value $pK_a' = 3.55_6$ for the first acidic dissociation constant of gluconic acid. The value reported includes the acid–lactone formation constants as defined below

$$K_a' = \frac{(H^+)(GH_4^-)}{(HGH_4)\left(1 + \frac{1}{K_{\delta GL}} + \frac{1}{K_{\gamma GL}}\right)} \quad (2)$$

where $K_{GL} = (HGH_4)/(GL)$ and (GL) is the concentration of the particular gluconolactone species. Substituting equation 2 into 1 and solving for the gluconate ion concentration for the case in which $(PbGH_{(4-x)})$ is small and equal approximately to 1 mM and the total gluconic acid species equals 0.100 M, we have

$$(GH_4^-) = \frac{0.1 - (PbGH_{(4-x)})}{\frac{(H^+)}{K_a'} + 1} = \frac{0.099K_a'}{(H^+) + K_a'} \quad (3)$$

The function log $C_{GH_4^-}$ *vs.* pH is plotted in Fig. 3B for the case where total gluconic acid species equals 0.1 M, using equation 3 and the value $pK_a' = 3.55_6$. The concentration of free gluconate ion concentration at any pH may be determined from this figure.

The general reduction reaction (6) may, for convenience, be written as the sum of two partial reactions

$$PbGH^{+(1-x)}_{(4-x)} + xH^+ = Pb^{++} + GH_4^- \quad (4)$$

$$Pb^{++} + Hg + 2e^- = Pb(Hg) \quad (5)$$

$$PbGH^{+(1-x)}_{(4-x)} + xH^+ + Hg + 2e^- = Pb(Hg) + GH_4^- \quad (6)$$

The equation of the wave, derived in the usual manner[5] with the substitution of eq. 3 for the concentration of the complexing ligand for the case in which total gluconic acid species equal 0.1 M, is

$$E_{d.e.} = \epsilon + 0.0296 \log \frac{Kk_a}{k_c} - 0.0296 \log \frac{0.099K_a'}{(H^+) + K_a'} - 0.0296(x)p\text{H} - 0.0296 \log [i/(i_d - i)] \quad (7)$$

where K is the equilibrium constant for reaction 4 and the other symbols have their usual significance.[5] The half-wave potential of the complex has the value

$$(E_{1/2})_c = \epsilon + 0.0296 \log \frac{Kk_a}{k_c} - 0.0296(x)p\text{H} - 0.0296 \log \frac{0.099K_a'}{(H^+) + K_a'} \quad (8)$$

Thus, if the function $(E_{1/2})_c + 0.0296 \log \{0.099K_a'/[(H^+) + K_a']\}$ is plotted *vs.* pH, a straight line should be produced the slope of which is $0.0296(x)$. This relation was plotted and the slope obtained was 0.0. That is, the quantity $(E_{1/2})_c + 0.0296$ log $\{0.099K_a'/[(H^+) + K_a']\}$ was found to be con-

(13) R. K. Cannan and A. Kibrick, THIS JOURNAL, **60**, 2314 (1938).

stant, independent of pH. This proves that the shift in half-wave potential is caused completely by the formation of gluconate and that no hydrogens enter into the over-all reduction equation. The general equation 4 is correctly written

$$PbGH_4^+ = Pb^{++} + GH_4^-$$

The positive charge on the complex is in agreement with migration studies.

Dissociation Constant of $PbGH_4^+$.—Equation 8 may be combined with the equation for the half-wave potential of a simple metal ion derived by von Stackelberg[14] and by Lingane.[15] The difference in half-wave potentials between complexed and uncomplexed lead becomes

$$(E_{1/2})_c - (E_{1/2})_s = 0.0296 \log \frac{Kk_s}{k_c} - 0.0296 \log \frac{0.099K_a'}{(H^+) + K_a'} - 0.0296(x)pH \quad (9)$$

An estimate of the dissociation constant of the complex formed in acidic solution, $PbGH_4^+$, may be made by solving equation 9 for pK. Substituting the ratio $(i_d)_s/(i_d)_c$ for k_s/k_c (all diffusion currents measured at the same concentration of lead), inserting the value $x = 0$, and rearranging the terms, we have

$$pK = \frac{(E_{1/2})_c - (E_{1/2})_s}{-0.0296} + \log \frac{(i_d)_s}{(i_d)_c} - \log \frac{0.099K_a'}{(H^+) + K_a'} \quad (10)$$

Table I gives several values of pK determined by use of equation 10.

TABLE I

DETERMINATION OF THE pK FOR $PbGH_4^+$ COMPLEX IN WEAKLY ACIDIC SOLUTIONS ($\mu = 0.1$)

pH	$\frac{(E_{1/2})_c - (E_{1/2})_s}{-0.0296}$	$\log \frac{0.099K_a'}{(H)^+ + K_a'}$	$\log \frac{(id)_s}{(id)_c}$	pK
2.40	0.43_8	−2.19	0.008	2.6
3.28	0.97_8	−1.47	.088	2.5
3.68	1.1_8	−1.25	.104	2.5
4.40	1.4_5	−1.06	.125	2.6
4.90	1.5_9	−1.02	.126	2.7
5.32	1.6_2	−1.01	.128	2.7

Av. $pK = 2.6 \pm 0.1$

Effect of Gluconate in Strongly Basic Solution.—The effect on the half-wave potential of changing the concentration of gluconate at various constant concentrations of sodium hydroxide was studied. Concentrations of sodium gluconate ranged from 0.008 to 0.100 M, while sodium hydroxide concentrations ranged from 0.1 to 3 M. The concentration of lead was 0.001 M in all cases. If one maintains the hydroxide concentration constant and plots the log of the excess uncomplexed gluconate (taking into account the concentration of gluconate produced at the surface of the d.m.e. as reduction proceeds) as a function of the half-wave potential, a straight line should be obtained whose slope is $0.0296(p)$, where p is the number of gluconate molecules per lead.[2a]

Figure 4 is a plot of the log of the free gluconate concentration *vs.* the half-wave potential for several hydroxide concentrations. A series of straight lines at the various concentrations of sodium hydroxide was obtained with an average slope corresponding to 0.91 ± 0.08 (= 1) gluconate per lead. In obtaining this average slope, the slope for 0.1 M sodium hydroxide solutions was not included, since these solutions contained up to 0.003% gelatin to suppress a small maximum. The value obtained for p from this curve (0.77) was not taken as significant since gelatin has an effect on the half-wave potential. The data for concentrations of sodium hydroxide greater than 0.1 M show that for solutions of lead containing 0.008 to 0.100 M sodium gluconate, the predominant species has a 1:1 ratio of lead to gluconate.

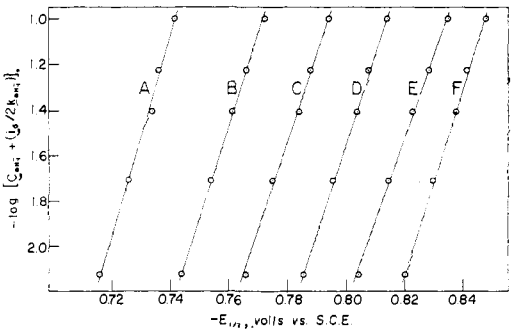


Fig. 4.—Effect of gluconate concentration on the half-wave potential of lead in strongly basic solution. The concentrations of sodium hydroxide are: A, 0.103 M; B, 0.248 M; C, 0.497 M; D, 0.996 M; E, 1.992 M; F, 2.989 M.

Effect of Hydroxide Concentration.—The effect on the half-wave potential of changing the hydroxide concentration at various constant gluconate concentrations was investigated. The ionic strength was adjusted to 3.0 with sodium perchlorate. Sodium gluconate concentrations varied from 0.008 to 0.06 M and sodium hydroxide concentration varied from 0.1 to 2.8 M. A plot of log (C_{OH^-}) *vs.* $E_{1/2}$ gave a series of approximately parallel straight lines for each gluconate concentration studied. The average slope was 0.0634 which corresponds to an experimental value of x equal to 2.14 hydroxide ions entering into the reduction reaction per lead.[2a] Apparently the reduction reaction is either

$$PbGH_2^- + 2H_2O + Hg + 2e^- = Pb(Hg) + GH_4^- + 2OH^- \quad (11)$$

or

$$Pb(OH)GH^-{}_3 + H_2O + Hg + 2e^- = Pb(Hg) + GH_4^- + 2OH^- \quad (12)$$

Reaction 11 is correct if the gluconate molecule acts as a tridentate ligand with the most likely bonding between the carboxyl group and the C_2 and C_4 hydroxyl groups (the hydrogens of these hydroxyl groups displaced by chelate formation). Reaction 12 is correct if the gluconate molecule acts as a bidentate ligand. Our experimental data will not differentiate between these two reactions.

Equilibrium Constants.—The "apparent equilibrium constant" for the reaction

$$\text{Complex} + yH_2O = Pb^{++} + GH_4^- + 2OH^- \quad (13)$$

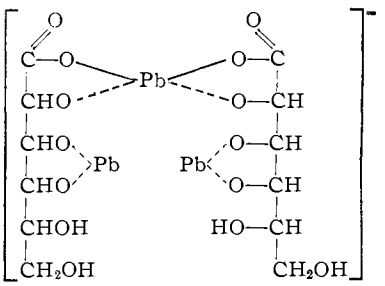
(14) M. von Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).
(15) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

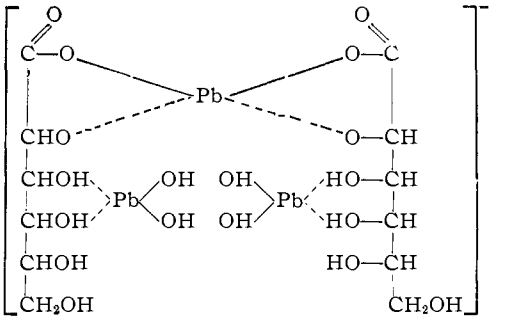
has been determined from polarographic data at ionic strengths from 3.0 to 0.15. The equation

$$pK = \frac{(E_{1/2})_c - (E_{1/2})_s}{-0.02957} - \log\left(C_{GH_4}^{-} + \frac{C_{complex}}{2}\right)(OH^-)^2 + \log\frac{(i_d)_s}{(i_d)_c} \quad (14)$$

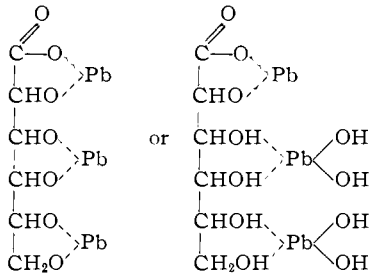
may be used to determine the pK for reaction 13.[2a] Five determinations of the pK were made in each case. The average pK value and the standard deviation is: $\mu = 3.0$, $pK = 16.39 \pm 0.05$; $\mu = 2.0$, $pK = 16.26 \pm 0.03$; $\mu = 1.0$, $pK = 16.17 \pm 0.05$; $\mu = 0.55$, $pK = 16.09 \pm 0.05$; $\mu = 0.30$, $pK = 15.92 \pm 0.06$; $\mu = 0.15$, $pK = 15.71 \pm 0.09$.

Probable Structure.—The evidence presented above suggests the following types of structures for the 3:2 complex present at pH 11.5. The state of hydration cannot be determined from our data.





The most probable structure of the 3:1 solid which precipitates at pH 11.5 is



Acknowledgment.—We wish to thank the Research Corporation for a grant-in-aid in support of this work. We also wish to thank Professor John C. Bailar, Jr., for reviewing the manuscript.

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Synthesis and Properties of Some Fluoro-bis-(ethylenediamine)-cobalt(III) Complexes[1-3]

BY WILLIAM R. MATOUSH AND FRED BASOLO

RECEIVED MARCH 19, 1956

A somewhat different approach to the synthesis of fluoroamminecobalt(III) salts is presented. Preparation of five new complexes is described and the isolation of optically active compounds containing a metal–fluoride bond is reported for the first time. Isolation of such optically active forms provides a proof of structure for three different pairs of geometric isomers. Reactions of *dextro*-$[Coen_2F_2]^+$ give no evidence for a Walden inversion type reaction as is known for *levo*-$[Coen_2Cl_2]^+$.

Extensive investigations[4] have been carried out on the synthesis and properties of chloroamminecobalt(III) complexes, whereas relatively few[5] studies are reported on the corresponding fluoro compounds. However, the role of fluoride ion in these complexes is of interest with regard to metal–ligand bonding in coördination compounds.[6] Magnetic data suggest that the cobalt(III)–fluoride bond is "ionic" in $[CoF_6]^{-3}$ but "covalent" in partially substituted cobalt(III) ammines. Except for the fact that the latter complexes are diamagnetic, little is known about the nature of the Co–F bond in these compounds. It is, therefore, the purpose of this paper to describe some of the properties of fluoro-bis-(ethylenediamine)-cobalt (III) complexes with specific reference to methods of synthesis, reactions and resolution of *racemic* compounds.

Experimental

Preparation of Compounds.—The fluoro-bis-(ethylenediamine)-cobalt(III) salts were generally prepared from the corresponding chloro or carbonato complexes. These starting materials were synthesized by standard procedures described in the literature.[4]

***trans*-Difluoro-bis-(ethylenediamine)-cobalt(III) Salts.**—The method of Seibt[5a] was used to prepare the bifluoride salt of this complex. However, large quantities of this com-

(1) Previous communication, W. R. Matoush and F. Basolo, THIS JOURNAL, **77**, 1072 (1955).

(2) Investigation supported by a National Science Foundation Grant (NSF-G58) and in part by a grant from the United States Atomic Energy Commission under Contract AT(11-1)-89-Project No. 2.

(3) Presented in part at the International Conference on Coördination Compounds in Amsterdam, April, 1955.

(4) "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie G. M. B. H., Berlin, 1930, Vol. 58B, pp. 1–376.

(5) (a) H. Seibt, Dissertation University of Zurich, 1913; (b) M. Linhard and M. Weigel, *Z. anorg. allgem Chem.*, **271**, 101 (1952).

(6) (a) W. C. Fernelius, *Rec. Chem. Progr. (Kresge Hooker Sci. Lib.)*, **2**, 17 (1950); (b) H. Taube, *Chem. Revs*, **50**, 69 (1952); (c) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).