TABLE III

STANDARD ENTHALPY AND ENTROPY CHANGE VALUES FOR THE STEPWISE FORMATION OF H_2A^+ AND CuA_2 FROM THEIR RESPECTIVE IONS

	$H^+ + A^- = HA$		$HA + H^+ = H_2A^+$		$Cu^{2+} + A^- = CuA^+$		$CuA^+ + A^- = CuA_2$	
Temp., °C.	$\Delta H°$, kcal./mole	$\Delta S°$, e.u.	$\Delta H°$, kcal./mole	$\Delta S°$, e.u.	$\Delta H°$, kcal./mole	$\Delta S°$, e.u.	$\Delta H°$, kcal./mole	$\Delta S°$, e.u.
10	−11.68	5.8			−5.38	20.8	−5.47	13.9
25	−11.30	7.4			−4.51	23.9	−5.24	14.3
	−10.8[a]		−0.6[a]					
	−11.0[b]		−0.8[b]					
40	−10.26	10.8			−3.99	25.3	−5.65	12.9
10–40	−10.4[c]	10.3[c]	−0.7[c]		−5.1[c]	21.8	−6.8[c]	9.0[c]
0–40	−10.6[d]	9.8[d]	−0.7[d]		−5.6[d]	20.7	−6.2[d]	10.7[d]

[a] Calorimetric results of J. M. Sturtevant, *J. Am. Chem. Soc.*, **64**, 726 (1942). [b] Results of Smith, *et al.*, see footnote *e* to Table II. [c,d] Results calculated by the temperature-coefficient method in this research and by Izatt, *et al.*,[2] respectively.

step than CuA^+ in the second step. It is significant that changes from one α-amino acid to another as the chelating group is changed do not affect to any large extent the observed $\Delta H_i°$ values and that the $\Delta H_1°$ and $\Delta H_2°$ values are nearly equal in all cases studied. The significantly lower value of K_2 compared to K_1 in the case of the Cu^{2+}–A^- system appears to be primarily a result of the markedly lower value of $\Delta S_2°$ compared to $\Delta S_1°$. This effect was also observed in the previous study,[3] the values of $\Delta S_2°$ and $\Delta S_1°$ in both studies being comparable in magnitude.

Acknowledgment.—The authors gratefully acknowledge the assistance of Mr. Dale Hammond in the design and construction of equipment and of Mr. Klint Stander in the performance of some of the titrations.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Proton Nuclear Magnetic Resonance Studies of Metal Gluconate Complexes. I. Lead(II) and Bismuth(III)

BY DONALD T. SAWYER AND JAMES R. BRANNAN

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Proton n.m.r. spectra have been recorded for the complexes formed by D-gluconic acid with Mg(II), Al(III), Zn(II), Mo(VI), Pb(II), and Bi(III) ions under alkaline conditions. Only the Pb(II) and Bi(III) complexes exhibit chemical shifts for the C–H protons of the gluconate anion that are significantly different from those observed for the free ligand. Mole ratio studies based on chemical shift changes establish that four metal gluconate species are formed with the Pb(II) and Bi(III) ions under alkaline conditions: (a) $Pb:GH_4 = 3:2$; (b) $Pb:GH_4 = 2:1$, (c) $Bi:GH_4 = 1:2$, and (d) $Bi:GH_4 = 1:1$. Formulas and structures are proposed for these four species on the basis of n.m.r. data and acid–base titrations. The data support the conclusion that the carboxylate group and the α, β, and γ alcoholic oxygens of the gluconate anion are the only donor groups involved in coordination.

Although the complexes formed between metal ions and D-gluconic acid have been extensively studied,[1] the nature of the metal–ligand bonding and the structures of the complexed species have not been well established. Proton nuclear magnetic resonance spectroscopy has been shown to be useful for structural and bonding studies of metal–EDTA complexes.[2,3] More recently the results of an n.m.r. study of gluconic acid, its salt, and its lactones as well as of other related hydroxy acids have been presented.[4] A brief study of the lead(II) and bismuth(III) tartrate complexes by n.m.r. has indicated the value of such studies for determining the bonding and formulas of hydroxy acid complexes.[5] On the basis of these latter two investigations, proton n.m.r. studies of metal gluconate complexes should be expected to provide a better understanding of the formulas, bonding, and the structures of the complex species. The present discussion summarizes the results of such a study for several metal gluconate complexes in aqueous solution.

Experimental Section

The proton n.m.r. spectra were recorded with a Varian A-60 high-resolution spectrometer equipped with a 60-Mc. oscillator. Chemical shifts were measured using tetramethylammonium chloride (TMA) as an internal reference. The resonance for this material is 3.177 p.p.m. downfield from 3(trimethyl silyl)1-propanesulfonic acid, sodium salt (TMS*), and the reported

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(1) D. T. Sawyer, *Chem. Rev.*, **64**, 633 (1964).

(2) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963).

(3) S. I. Chan, R. J. Kula, and D. T. Sawyer, *ibid.*, **86**, 377 (1964).

(4) D. T. Sawyer and J. R. Brannan, *Anal Chem.*, in press..

(5) J. R. Brannan and D. T. Sawyer, *Inorg. Chem.*, **4**, 1070 (1965).

resonances can be converted to this reference by adding the difference. The tetramethylammonium chloride reference has the advantage of having a constant chemical shift, independent of pH, which is close to the chemical shifts measured for the gluconate complexes. This permitted smaller and more sensitive sweep widths than would have been possible by using TMS*.

Sample solutions were prepared by dissolving the metal salt (either the chloride or the nitrate) into a 1 *F* D-glucono-δ-lactone solution. The latter solution was prepared with deuterium oxide (D_2O) because of the close proximity of the gluconate resonances to the resonance for H_2O. The sample solutions were adjusted to the desired pH or alkalinity with KOH pellets because of the smaller effect of potassium ion on pH measurements with a glass electrode. pH measurements were made with a Leeds and Northrup pH meter equipped with a high-range glass electrode; the meter was standardized with N.B.S. buffers. Because the sample solutions were prepared with D_2O the indicated pH value should be corrected by the expression[6]

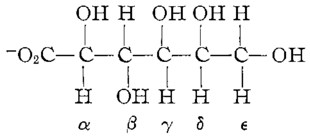
$$\text{pD} = \text{“meter reading”} + 0.40$$

This has not been done because the n.m.r. sample probe was operated at 40° and because of the approximate nature of pH measurements in alkaline solutions. Thus, the reported pH values are approximate, but they are meaningful in a relative sense.

The gluconate solutions were prepared from D-glucono-δ-lactone which was obtained from Chas. Pfizer and Co. In some cases this material was first recrystallized from solutions of ethylene glycol monomethyl ether, but no significant change was noted in the n.m.r. spectra relative to those recorded for the lactone as received. All other materials were reagent grade and were used without further purification.

Results

In the previous paper of this series[4] the proton n.m.r. spectra and chemical shift assignments for the gluconate anion are discussed. These assignments have been used in the present investigation and are the basis for determining the effect of metal ion coordination upon the n.m.r. spectrum for the gluconate anion. The structure for the anion of D-gluconic acid can be represented as



$$\begin{array}{ccccccccccc} & & \text{OH} & & \text{H} & & \text{OH} & & \text{OH} & & \text{H} \\ & & | & & | & & | & & | & & | \\ {}^{-}\text{O}_2\text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C}-\text{OH} \\ & & | & & | & & | & & | & & | \\ & & \text{H} & & \text{OH} & & \text{H} & & \text{H} & & \text{H} \\ & & \alpha & & \beta & & \gamma & & \delta & & \epsilon \end{array}$$

GH_4^-

with the several kinds of C–H protons identified by Greek letters. The anion is usually represented by GH_4^-, where the four protons refer to the four hydrogens on the secondary alcohol groups.[1]

The chemical shifts for the C–H protons of the gluconate anion are tabulated in Table I for a series of 1 *F* 1:1 metal gluconate solutions at pH 13.5. The first line is for the potassium salt and should represent the chemical shifts for the free anion; these do not change from pH 7 to pH 14. From the data in this table it is evident that addition of Mg(II), Zn(II), or Mo(VI) ions to a pH 13.5 gluconate solution has an insignificant effect upon the chemical shifts. The only evidence of any metal–ligand interaction is an increase in the line widths.

TABLE I

CHEMICAL SHIFTS FOR THE C–H PROTONS OF 1 *F* 1:1 METAL GLUCONATE SOLUTIONS AT pH 13.5.

	δ *vs.* TMA, p.p.m.				
Metal ion	α	β	γ	δ	ε
K(I)	0.983	0.80	0.583	0.583	0.583
Mg(II)	0.987	0.863	0.567	0.567	0.567
Al(III)	0.889	0.750	0.533	0.533	0.533
Zn(II)	0.975	0.833	0.580	0.580	0.580
Mo(VI)	0.975	0.813	0.510	0.510	0.510
Pb(II)	1.917	1.500	1.050	0.60	0.60
Bi(III)	2.350	2.050	1.700	0.817	0.817

At neutral pH conditions the spectrum for a 1:1 magnesium gluconate solution becomes extremely broad and unresolved. At pH 11.5 the α and β protons are shifted downfield to the maximum extent with chemical shifts of 1.10 and 0.943 p.p.m., respectively. As the pH is increased further the chemical shifts again move upfield to their values in Table I.

In the case of the zinc gluconate solution, the n.m.r. spectrum becomes so broad at pH 8.5 that it is not observable and even at pH 12.8 the peaks are merged. Above pH 14 the spectrum for zinc gluconate appears identical with that for the free gluconate anion. The molybdenum gluconate system does not exhibit any significant chemical shift changes with changes in pH; however, the resonance lines become narrower as the pH is increased.

The resonance lines for the 1:1 aluminum(III) gluconate solution are broad at all alkaline pH values and move upfield with increasing pH. When the solution is made 2 *F* in KOH only two peaks are observed for the aluminum complex, one at 0.710 p.p.m. and the other at 0.457 p.p.m.; the relative areas for the two peaks are 1:2, respectively. The metal–ligand interaction appears to have the greatest effect upon the α and β protons, but the broad nature of the spectrum precludes any further conclusions.

The data in Table I for the lead(II) and bismuth(III) gluconate solutions indicate extensive interaction between the metal ion and the ligand. Variation of the mole ratio of metal to ligand for these two systems does not cause new peaks to appear in the n.m.r. spectrum for the gluconate ion, but it does cause several of the peaks to shift.

Although a complex containing three lead ions per gluconate ion has been reported,[7] attempts to prepare solutions of such a complex under alkaline conditions have not been successful because of precipitation. However, solutions containing 0.5 *F* gluconate ion and lead ion concentrations up to 1.0 *F* can be prepared under alkaline conditions without precipitation. The results for a mole ratio study at pH 13.5 upon the chemical shifts for the gluconate C–H protons are shown in Figure 1. The chemical shifts for the α, β, and γ C–H protons shift downfield in a semilinear fashion as the mole ratio of lead(II) ion to gluconate ion is increased, up to a ratio of 1.5; above this mole ratio the chemical shifts become independent. The rate of downfield shift with increasing mole ratio is greater for the α and γ protons than it is for the β proton. As the mole ratio is increased above 1.0 the chemical shifts

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(6) K. Mikkelson and S. O. Nielson, *J. Phys. Chem.*, **64**, 632 (1960).

(7) R. L. Pecsok and R. S. Juvet, Jr., *J. Am. Chem. Soc.*, **78**, 3967 (1956).

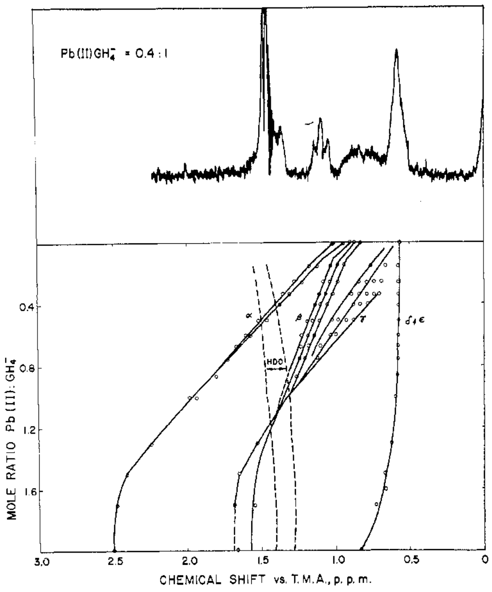


Figure 1.—Chemical shifts for the C–H resonances of the gluconate anion as a function of the mole ratio of lead(II) ion. Solution 1 F in gluconate ion and adjusted to pH 13.3.

for the δ and ε protons begin to shift downfield and the rate of shift becomes rapid above a mole ratio of 1.5.

The effects of solution pH upon the chemical shifts for the C–H protons of the gluconate ion are shown in Figures 2 and 3 for the 1:2 and 1:1 lead gluconate systems, respectively. For the 1:2 solution, the chemical shifts for the α and γ protons are shifted to their maximum downfield extent at pH 12.5; above this pH they begin to shift upfield. As the solution is made more alkaline than pH 12.5 the chemical shift for the β proton begins to shift downfield until its chemical shift becomes the same as that for the α proton when the solution is 3 M in hydroxide ion. Under these conditions of high alkalinity, the chemical shift for the γ proton moves upfield to a point where its value is almost the same as that for the gluconate anion (Table I). These same effects with increasing solution alkalinity are observed for the 1:1 lead gluconate system and are illustrated by Figure 3. However, the α and γ protons are obscured by the HDO resonance at the lower pH values. The 1:1 complex begins to precipitate at pH 14.3, which precludes more alkaline studies.

A pH study also has been made of the 2:1 lead gluconate system. The chemical shift for the α proton resonance remains constant at 2.5 p.p.m., but the remaining resonances become broad and merge together to give one broad band between 0.5 and 1.5 p.p.m.

A potentiometric acid–base titration of the 1:1 lead gluconate system indicates that two hydroxide groups are added per lead ion in the complex at pH 13.3. The titration consisted of taking a 75-ml. sample containing 25 mmoles of $Pb(NO_3)_2$ and 25 mmoles of D-gluceno-δ-lactone and titrating with 5.00 F KOH to pH 13.3 (about 100 mmoles was required). A 90-ml. solution of H_2O was titrated to pH 13.3 and served as the blank (approximately 25 mmoles of base was required).

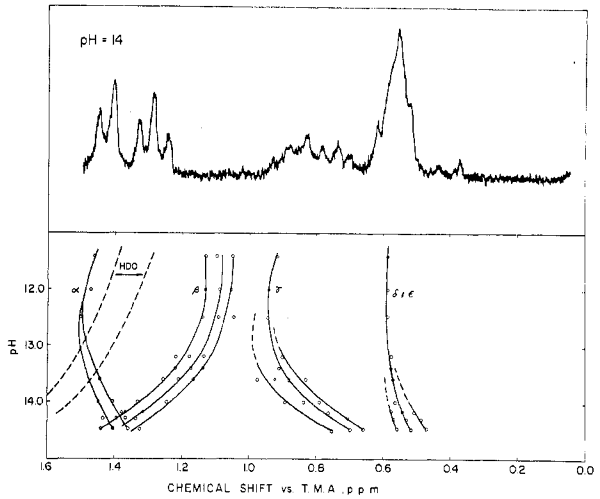


Figure 2.—Chemical shifts for the C–H resonances of the gluconate anion as a function of pH for a 1:2 solution of lead(II) gluconate. Solution 1 F in gluconate ion.

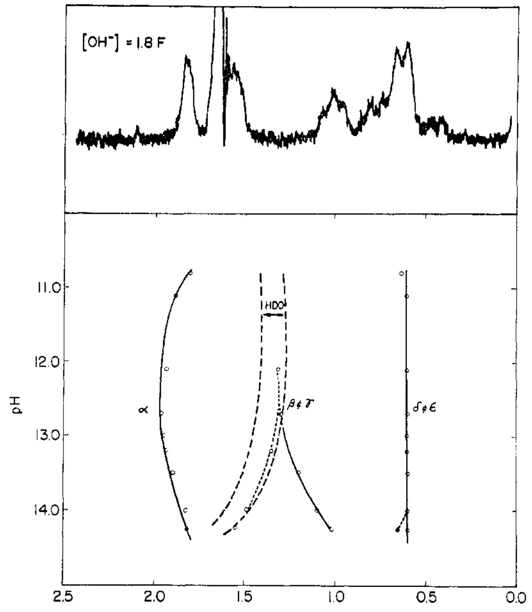


Figure 3.—Chemical shifts for the C–H resonances of the gluconate anion as a function of pH for a 1:1 solution of 1 F lead(II) gluconate.

Thus, the net titration consists of adding 75 mmoles of base to the 25-mmole sample; 25 mmoles is consumed neutralizing the lactone leaving a net of 50 mmoles of base being added to the complex.

The bismuth gluconate complex system has been studied in a similar manner to the n.m.r. studies for the lead gluconate complexes. The results of a mole ratio study at pH 13.8 are shown in Figure 4. Again the chemical shifts for the various C–H protons of the gluconate ion are plotted as a function of the mole ratio of bismuth(III) ion to gluconate ion. The α and β protons shift downfield at a much greater rate than the γ proton as the mole ratio of bismuth ion is increased. There is a significant discontinuity at a mole ratio of 0.5 for the α and β chemical shifts. As with the lead

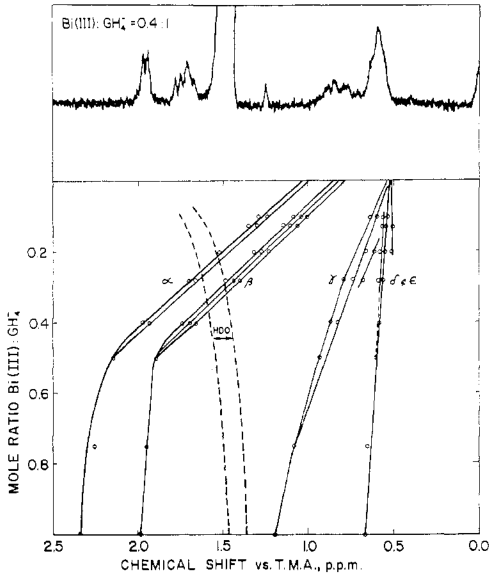


Figure 4.—Chemical shifts for the C–H resonances of the gluconate anion as a function of the mole ratio of bismuth(III) ion. Solution 1 *F* in gluconate ion and adjusted to pH 13.8.

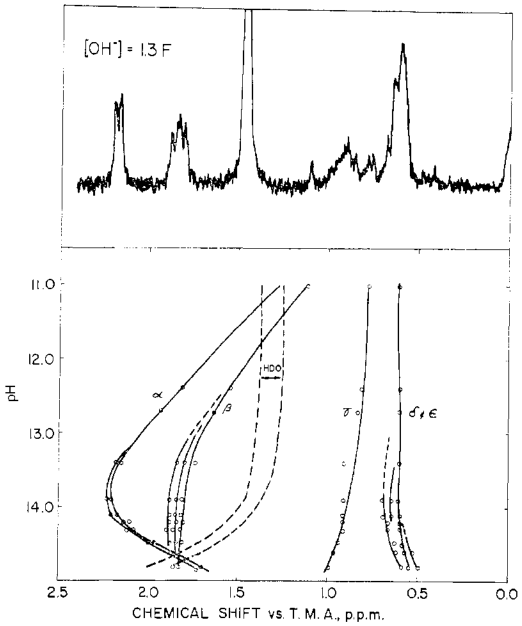


Figure 5.—Chemical shifts for the C–H resonances of the gluconate anion as a function of pH for a 1:2 solution of bismuth(III) gluconate. Solution 1 *F* in gluconate ion.

complexes the δ and ε protons are not affected significantly by the addition of the bismuth ion.

The effect of solution pH upon the chemical shifts for the 1:2 and 1:1 bismuth gluconate complexes is shown in Figures 5 and 6, respectively. As with the lead complexes, the α proton shifts downfield with increasing pH and reaches its maximum shift at pH 13.9 for the 1:2 bismuth complex and at 14.3 for the 1:1 bismuth complex. In the case of the 1:2 system the β proton shifts downfield up to a pH of 13.3 and then remains constant at higher pH values. Above pH 14 the γ proton begins to shift downfield. For the 1:1 complex all of the gluconate protons tend to shift downfield with increasing pH; this is particularly pronounced for the β and γ protons.

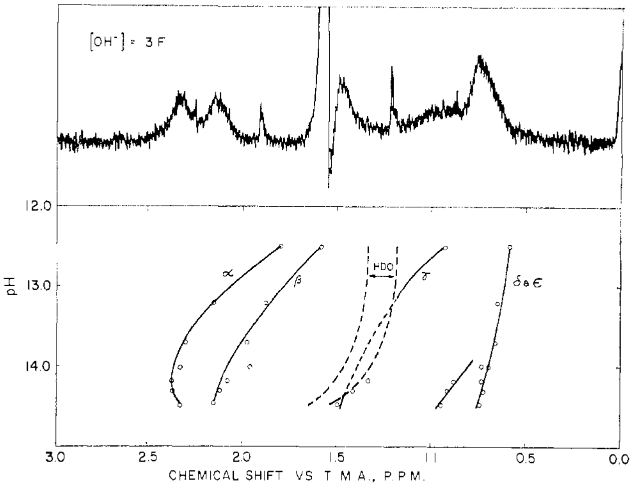


Figure 6.—Chemical shifts for the C–H resonances of the gluconate anion as a function of pH for a 1:1 solution of 1 *F* bismuth(III) gluconate.

Potentiometric acid–base titrations of the 1:2 and 1:1 bismuth gluconate systems indicate that four hydroxides are added per bismuth ion at pH 13.3 for each of the two systems. These titrations consisted of taking 75-ml. samples containing 25 mmoles of Bi$(NO_3)_3$ and either 25 or 50 mmoles of D-glucono-δ-lactone and titrating with 5.00 *F* KOH to pH 13.3 (about 150 mmoles was required for the 1:1 system and about 185 mmoles for the 1:2 system). Blank titrations were run on 100-ml. and 110-ml. H_2O solutions to the same pH (about 25 and 30 mmoles was required, respectively). Thus, for the 1:1 system the net titration consists of 125 mmoles of base being added to the 25-mmole sample; 25 mmoles is consumed neutralizing the lactone leaving a net of 100 mmoles of base being added to the complex. For the 1:2 system the net titration is about 155 mmoles of base per 25 mmoles of bismuth(III); 50 mmoles is required to neutralize the 50 mmoles of lactone leaving a net of 105 mmoles of base being added to the complex.

The effect of temperature upon the n.m.r. spectra for the lead(II) and bismuth(III) gluconate complexes also has been studied. Qualitatively an increase in temperature causes the resonance lines to become sharper and produces a chemical shift change similar to that resulting from a small increase in pH. At pH values above pH 14 this effect is enhanced. The temperature effect upon chemical shifts is such that a change from 25 to 40° would not change the chemical shifts more than 0.1 p.p.m. for any of the gluconate C–H protons.

Attempts to study the gluconate complexes formed with the ions of barium, calcium, and cadmium have not been successful because of their limited solubility. Because the cobalt(III) gluconate complex might be expected to be less labile than the lead or bismuth complexes, efforts have been made to study it by n.m.r. The barium salt of the cobalt(III) gluconate complex, synthesized by the method of Traube,[8] has been used to prepare the cobalt(III) solution. The broad, smeared nature of the n.m.r. spectrum of this solution indicates that significant decomposition and formation of cobalt(II) occurs. As a result meaningful studies of alkaline cobalt(III) gluconate solutions have not been possible.

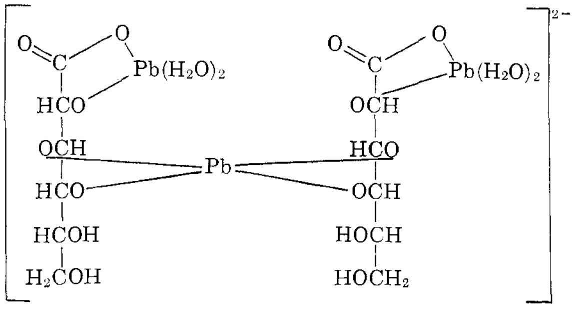
Discussion and Conclusions

The significant downfield shifts for the C–H protons of the gluconate ion in the presence of lead(II) and bismuth(III) ions indicate that there are strong interactions between these metal ions and the ligand. The data of Figures 2, 3, 5, and 6 support the conclusion that these interactions have their maximum extent between pH 12.5 and pH 14. Because additional resonance lines are not observed when excess ligand is present, the metal–ligand exchange rate must be rapid. Thus the observed chemical shifts are the weighted average for the free ligand and the coordinated ligand.

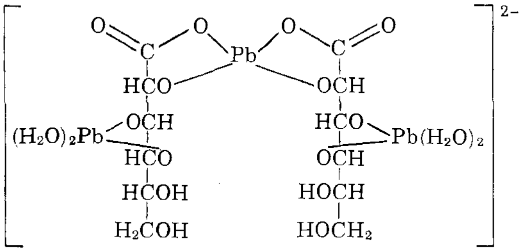
Lead(II) Complexes.—The n.m.r. data of Figures 1, 2, and 3 plus the pH titrations for the 1:1 lead(II) gluconate system permit several conclusions to be made concerning the formulas and bonding for the several complexes. The discontinuity in Figure 1 for the α and γ protons supports the conclusion that a stable lead complex is formed with three lead ions per two gluconate ions. Because a solution containing two lead ions per gluconate ion is stable, such a complex also must be formed. The more pronounced downfield shifts for the α and γ protons with increasing metal–ligand mole ratios indicate that the α and γ alcoholic oxygens are involved in bonding to the lead ion. The slower rate of downfield shift for the β proton may imply that the β oxygen is not involved in bonding, but is shifting downfield because of the bonding by the α and γ oxygen atoms. The early work of Isbell based on measurements of optical rotation supports the conclusion that the α oxygen is bonded to the lead ion.[9] The data of Figures 2 and 3 indicate that at pH values above pH 14 the β oxygen apparently displaces the γ oxygen in its bonding to the lead ion. Also, the upfield shift of the α proton implies a change in its environment with increasing pH; this could be a weaker interaction between the α oxygen and the metal ion or it could be because a hydroxide ion is displacing the carboxylate ion from its bonding to the metal ion. The latter possibility seems more likely and is consistent with the conclusions of others regarding metal gluconate complexes in strongly alkaline solutions.[10–12]

Reference to Figure 1 indicates that for mole ratios of lead to gluconate above 1.0 some interaction between the metal ion and the δ and ϵ oxygens may be developing. However, the change in chemical shift is much smaller and the rate of change does not become significant until the mole ratio reaches 2.0.

Because the acid–base titration of a 1:1 lead gluconate solution to pH 13.3 requires two hydroxide ions per lead ion in the complex and the n.m.r. data indicate that the complex contains three lead ions per two gluconate ligands, the formula for the complex at this pH is concluded to be $[Pb_3(GH_4)_2(OH)_6]^{2-}$. Two structures for the 3:2 complex which are consistent with the formula and the data of Figures 2 and 3 are



and



The second structure is roughly the same as that proposed by Pecsok and Juvet.[7]

The solubility of lead ion in alkaline gluconate solutions up to a mole ratio of 2.0 supports the conclusion that a stable complex is formed containing two lead ions per gluconate ion. The n.m.r. data indicate that for such a species the two lead ions probably are coordinated by the carboxylate group plus the α, β, γ, and possibly δ oxygens of the ligand.

Bismuth(III) Complexes.—The extensive downfield shift of the α and β C–H resonances with increasing bismuth ion concentrations (Figure 4) strongly supports the conclusion that the α and β gluconate oxygens are coordinated to the bismuth ion. The data of Figure 4 also indicate that two stable complexes are formed in alkaline gluconate solutions; one containing one bismuth ion per two gluconate ions and the other having a mole ratio of one. The acid–base titrations for these two complexes indicate that their formulas at pH 13.3 are $[Bi(GH_4)_2(OH)_4]^{3-}$ and $Bi(GH_4)(OH)_4{}^{3-}$.

On the basis of the n.m.r. data and the formulas for the two complexes a reasonable structure for the 1:2 complex involves bonding by the carboxylate group plus the α and β oxygens of each of the two gluconates to the bismuth ion (making it six-coordinate). Thus the four hydroxide ions are consumed in neutralizing the α and β alcoholic protons. For the 1:1 complex a structure consistent with the data involves bonding by the carboxylate group plus the α and β oxygens of the gluconate. Two hydroxide ions are used to neutralize the two alcoholic protons and the other two are bonded to the bismuth ion together with a water molecule to

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(8) W. Traube, F. Kuhbier, and W. Schroder, *Ber.*, **69B**, 2655 (1936).

(9) H. S. Isbell, *J. Res. Natl. Bur. Std.*, **14**, 305 (1935).

(10) R. L. Pecsok and J. Sandera, *J. Am. Chem. Soc.*, **77**, 1489 (1955).

(11) Y. A. Fiaklov and N. G. Peryshkiva, *Zh. Neorgan. Khim.*, **2**, 749 (1957).

(12) Y. A. Fiaklov and N. G. Peryshkiva, *ibid.*, **3**, 1578 (1958).

make the bismuth six-coordinate. There is a possibility that one of the hydroxide groups is displaced, at least in part, by the γ gluconate oxygen in the 1:1 complex; this appears to be true especially at high pH values. At pH values above pH 14 the carboxylate groups in the 1:1 complex appear to be displaced by hydroxide ions; this apparently does not occur to a significant extent for the 1:1 complex (Figure 6).

In general the interactions between the gluconate ion and lead and bismuth ions appear quite similar to those observed for the tartrate ion.[5] Under alkaline conditions bonding to the alcoholic oxygens is accomplished by displacement of the proton. Of the soluble diamagnetic ions studied only lead and bismuth exhibit coordination by the alcoholic oxygens. However, a number of paramagnetic ions are known to be complexed strongly by gluconate ion,[1] especially iron(III), copper(II), and the rare earths. Unfortunately proton n.m.r. studies are not possible because of the strong relaxation effects upon the line widths. However, the donor groups involved in bonding to the paramagnetic ions can reasonably be concluded to be the same as those observed for the lead and bismuth ions under similar solution conditions. Thus, a general conclusion is that the α, β, and γ oxygen atoms of the gluconate ion together with the carboxylate group are the effective donor groups for complexation under alkaline conditions.

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Contribution from the Chemistry Department,
Nagoya University, Chikusa, Nagoya, Japan

Broad-Line Proton Magnetic Resonance Spectra of Dichloro(1,2,4-triazole)copper(II) and Bis(1,2,4-triazolato)copper(II)

By MOTOMICHI INOUE and MASAJI KUBO

Received June 18, 1965

The broad-line p.m.r. spectrum of dichloro(1,2,4-triazole)copper(II) consists of two absorptions of intensity ratio equal to 2:1, indicating the existence of two kinds of nonequivalent hydrogen atoms in crystals in agreement with the results of X-ray analysis. The spectrum of bis(1,2,4-triazolato)copper(II) comprises two absorptions of equal intensity, indicating the existence of two kinds of nonequivalent hydrogen atoms in crystals. From the observed field shifts due to Fermi contact hyperfine interaction, the spin densities on atoms in the nitrogen heterocycles were evaluated. On the basis of this information, along with magnetic data obtained earlier, possible structures are proposed for this compound.

Introduction

In a preceding paper,[1] we have reported the results of measurements on the magnetic moments of a variety of copper(II) complexes having nitrogen heterocycles as ligands. It was found that whereas a normal magnetic moment of 1.81 B.M. was observed for dichloro(1,2,4-triazole)copper, bis(1,2,4-triazolato)copper(II) shows a subnormal magnetic moment, 1.66 B.M., at room temperature, suggesting the existence of copper atoms magnetically coupled in pairs. In order to obtain further information on the structure of these complexes, we have recorded the broad-line p.m.r. spectra and evaluated the spin densities on atoms in the nitrogen heterocycles from the observed field shifts due to Fermi contact hyperfine interaction.

Experimental Section

The powdered crystals of dichloro(1,2,4-triazole)copper(II) and bis(1,2,4-triazolato)copper(II) were prepared as described in a previous report.[1]

The p.m.r. spectra of these compounds were recorded at 24° by means of a Model JNS-B broad-line n.m.r. spectrometer from Japan Electron Optics Laboratory Co. operating at 35.45 Mc. with an amplitude of magnetic field modulation of 1.0 oersted. Since high-resolution chemical shifts are trivial in broad-line n.m.r. spectra, any diamagnetic hydrogen-containing compounds may be used as a reference. We employed water as an external standard. A small amount of copper(II) sulfate was dissolved in it in order to facilitate spin relaxation.

Results

The observed absorption derivative curves are shown in Figure 1. The curve of dichloro(1,2,4-triazole)copper(II) is asymmetric and can be decomposed into two simple derivative curves of intensity ratio equal to 2:1 as shown in Figure 1a. The curve observed for bis(1,2,4-triazolato)copper(II) also is composite and is made up of two simple curves of equal intensity superposed on each other. The observed nuclear resonance field shifts $\Delta H/H$ are shown in Table I.

Discussion

The X-ray crystal analysis of dichloro(1,2,4-triazole)copper(II) has been carried out by Jarvis,[2] who found that all 1,2,4-triazole molecules are equivalent in the crystal and that two neighboring nitrogen atoms in a molecule of the nitrogen heterocycle are coordinated

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(1) M. Inoue, M Kishita, and M. Kubo, *Inorg. Chem.*, **4**, 626 (1965).

(2) J. A. J. Jarvis, *Acta Cryst.*, **15**, 964 (1962).