

Carbohydrate Complexes with Lead(II) Ion. Interaction of Pb(II) with β -D-Glucurono-6,3-lactone, D-Glucono-1,5-lactone, and Their Acid Anions and the Effects of Metal Ion Binding on the Sugar Hydrolysis

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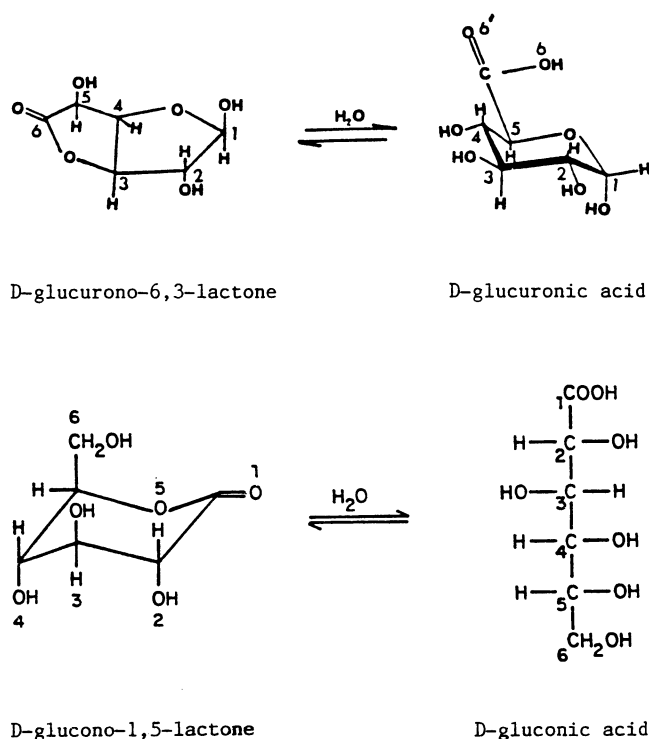
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The interaction of Pb(II) ion with β -D-glucurono-6,3-lactone, D-glucuronic acid, D-glucono-1,5-lactone, and their acid anions has been investigated in aqueous solution and solid compounds of the type Pb(D-glucurono-6,3-lactone)(NO₃)₂, Pb(D-glucuronic acid)(NO₃)₂, Pb(II)-D-glucuronate, Pb(D-glucono-1,5-lactone)(NO₃)₂, and Pb(II)-D-gluconate have been isolated. These compounds are characterized by means of FT-IR, ¹H and ¹³C NMR spectroscopy and molar conductivity measurements. Among these Pb-sugar complexes, the crystal structure of the Pb(II)-D-gluconate is known through X-ray diffraction measurements, in which the lead(II) ion is hexacoordinated, binding to four D-gluconate anions via a carboxylate oxygen and an α -hydroxyl group of the two anions (chelation) and to a carboxylate oxygen atom of the other two sugar anions (unidentately). Spectroscopic evidence suggested that in the Pb-lactone or Pb-acid adducts, the metal ion could be bonded to a lactone or acid molecule through one of the carbonyl oxygen atom and other sugar donor group as well as to two bridging nitrate groups. In the Pb(II)-D-gluconate, the metal ion could be bonded to four sugar moieties (similar to that of the Pb(II)-D-gluconate) via a carboxylate oxygen atom and other sugar donor group of the two anions and to a carboxylate oxygen atom of the other two acid anions, resulting into a hexa-coordinated lead(II) ion. The β -anomer sugar configuration is predominant in the free D-glucurono-6,3-lactone, D-glucuronic acid, D-gluconate anion and in these Pb-sugar complexes.

The highly toxic effect of lead on the environmental pollution have been known for some years,¹⁾ and correlations between lead poisoning^{2,3)} and its carcinogenic action in animals have been established.⁴⁾ It has been also demonstrated that the injected lead in rats accumulates in the cell nuclei.⁵⁾ In recent years, the stabilizing or destabilizing effects of the Pb(II) ion interaction on the double-helix structure of DNA have been investigated and the mode of Pb-DNA binding has been the subject of several studies.^{6–8)} Sugar is a part of nucleic acids and lead-sugar interaction could have biological importance. On the other hand, D-glucurono-6,3-lactone and D-glucono-1,5-lactone show biological properties and are readily hydrolyzed to D-glucuronic and D-gluconic acid in aqueous solution (Scheme 1).

In our recent report, it was shown how the silver nitrate complexes with the free β -D-glucurono-6,3-lactone, D-glucuronic acid, and D-glucono-1,5-lactone in aqueous solutions, while the silver acetate facilitates the lactone hydrolysis and the acid ionization.^{9–11)} Similarly, the alkaline earth metal ions (Mg²⁺ and Ca²⁺) coordinate with D-gluconate anion in aqueous solutions, whereas in ethanolic solution, the binding of these metal ions to the free lactone is preferred.¹²⁾ In this work, we describe the Pb(II) ion interaction with β -D-glucurono-6,3-lactone, D-glucuronic acid, and D-glucono-1,5-lactone, in aqueous solution and the isolation and characterization of the complexes formed, using FT-IR, ¹H and ¹³C NMR spectroscopy and molar conductivity measurements, that have not been reported so far. Furthermore, the effects of metal ion binding on the sugar hydrolysis have been discussed here.



Scheme 1.

Experimental

Materials and Methods. β -D-Glucurono-6,3-lactone, D-glucuronic acid, and D-glucono-1,5-lactone were purchased from Aldrich Chemical Co., and were used as supplied. Other chemicals were reagent grade and were used without further purification.

Synthesis of Pb-Sugar Adducts. The Pb-lactone adducts

Table 1. Analytical Data for Pb-Sugar Complexes

Compound	Calcd(Found)		
	%Pb	%C	%H
Pb(<i>D</i> -glucurono-6,3-lactone)(NO ₃) ₂	40.93 (39.90)	14.25 13.95	1.58 1.70
Pb(<i>D</i> -glucuronic acid)(NO ₃) ₂	39.43 (38.80)	13.17 13.55	1.91 1.75
Pb(<i>D</i> -glucuronate) ₂	34.90 (33.55)	24.44 23.80	3.05 2.90
Pb(<i>D</i> -glucono-1,5-lactone)(NO ₃) ₂	40.66 (39.70)	14.15 13.85	1.97 2.10
Pb(<i>D</i> -gluconate) ₂	34.46 (33.80)	24.20 23.50	3.69 3.85

were prepared by the addition of Pb(NO₃)₂, 1 mmol in H₂O (20 ml) to a solution of the free lactone 1 mmol in H₂O (10 ml). The solution mixtures were left at room temperature for a period of 48 h under slow evaporation and then ethanol-acetone (50/50) was used to bring down the white precipitate (avoid heating the solution, due to rapid lactone hydrolysis and acid ionization). This was filtered off and washed with acetone several times and dried over CaCl₂. The Pb-acid adducts were also prepared in a similar fashion, using *D*-glucuronic acid instead of the lactone and using ethanolic solution to bring down the metal-acid precipitate. The analytical results given in Table 1, showed the composition of the type Pb(*D*-glucurono-6,3-lactone)(NO₃)₂, Pb(*D*-glucuronic acid)(NO₃)₂, and Pb(*D*-glucono-1,5-lactone)(NO₃)₂. The Pb-lactone adducts are very hygroscopic and should be kept in a desiccator over CaCl₂.

Synthesis of Pb-Sugar Salts. The Pb-sugar salts were prepared by the addition of the equimolar amount of the PbCO₃ and the lactone or acid in H₂O (50 ml) and the mixtures were heated up till all the lead carbonate was dissolved. After cooling down the solution to room temperature, ethanol was used to precipitate the white Pb-sugar salt. This was filtered off and washed with ethanol several times and dried over CaCl₂. The analytical data given in Table 1, showed the composition of Pb(*D*-gluconate)₂ and Pb(*D*-glucuronate)₂. The Pb-sugar salts synthesized here, are very soluble in water, but they are not soluble in common organic solvents.

Physical Measurements. The infrared spectra have been recorded on a NICOLET 5DXB Fourier Transform infrared instrument with DTGS detector. The spectra were taken as KBr pellets with a resolution of 2–4 cm⁻¹. The ¹H NMR spectra were recorded with a Varian XL-200 instrument in D₂O solution containing DSS as reference. The ¹³C NMR spectra have been recorded on a Bruker WH-80 instrument in D₂O solution containing dioxane as reference. Conductance measurements were carried out at room temperature in aqueous solution (10⁻³ mol dm⁻³) with a conductivity meter type CDM2e (Radiometer, Copenhagen).

Results and Discussion

FT-IR Spectra. The infrared spectra of the free *D*-glucurono-6,3-lactone, *D*-glucuronic acid, and *D*-glucono-1,5-lactone and their lead complexes have been recorded in the region of 4000–500 cm⁻¹ and a comparison has been made with those of the structurally identified *D*-glucuronate-CaBr·3H₂O,¹³⁾ Mn-

(II)-*D*-gluconate·2H₂O¹⁴⁾ and the corresponding Ag-sugar compounds^{9–11)} and the results of the spectral analysis will be discussed below.

Sugar OH Stretching Vibrations and Lead(II) Binding. The assignments of the infrared vibrational frequencies of the free *D*-glucurono-6,3-lactone, *D*-glucuronic acid, and *D*-glucono-1,5-lactone were reported earlier.^{9–12)} The free lactone and acid OH stretching vibrations appeared as several strong and broad absorption bands in the region of 3500–3200 cm⁻¹ of their spectra^{9–12)} and exhibited considerable intensity changes and shifting towards lower frequencies, on sugar metalation or acid ionization. The observed spectral changes in this region, are related to the participation of sugar OH group in lead-sugar binding. Similar trends were observed in the IR spectra of the structurally known *D*-glucuronate-CaBr·3H₂O and Mn(II)-*D*-gluconate·2H₂O, where sugar bindings were found to be via sugar OH groups as well as the carboxylate anion.^{13–15)}

Lactone Carbonyl Stretching Vibrations and Lead(II) Ion Binding. Drastic spectral changes were observed for each sugar carbonyl stretching vibration, upon lead ion interaction, which will be dealt with separately.

***D*-Glucurono-6,3-lactone.** The carbonyl stretching vibration of the free *D*-glucurono-6,3-lactone was observed as a strong band at 1758 cm⁻¹ and exhibited shifting and splitting at 1760 and 1757 cm⁻¹, in the spectrum of the Pb(*D*-glucurono-6,3-lactone)(NO₃)₂ adduct (Fig. 1). The shifting and splitting of the lactone C=O stretching vibration are related to the direct metal-carbonyl binding. Similar spectral changes were observed for the carbonyl stretching vibration, in the IR spectra of the AgNO₃, AgClO₄, and alkaline earth metal halide (Mg²⁺ and Ca²⁺) adducts with *D*-glucurono-6,3-lactone molecule, where metal sugar binding was concluded to be through the carbonyl oxygen atom.^{11,12)} The carbonyl stretching vibration of the free *D*-glucuronic acid was observed at 1709 cm⁻¹ and showed shifting and splitting at 1758 and 1730 cm⁻¹, in the spectrum of the Pb(*D*-glucuronic acid)(NO₃)₂ adduct (Fig. 1). The observed changes for the carbonyl group are due to the participation of the acid C=O group in metal ligand bonding, in the Pb(*D*-glucuronic acid)(NO₃)₂ compound. Similar trends were observed in the spectrum of the Ag(*D*-glucuronic acid)(NO₃) adduct, where metal-acid binding was suggested to be through the acid carbonyl oxygen atom.¹¹⁾ It should be noted that, one of the components of the C=O stretching vibration at 1758 cm⁻¹ in the spectrum of the Pb-acid adduct bears similarity to that of the free lactone (1758 cm⁻¹) or to that of the lactone at 1757 cm⁻¹, in the Pb-lactone adduct (Fig. 1). This can lead to the question of the purity of the Pb-acid compound that might be contaminated with the free lactone or Pb-lactone adduct (since the reaction has been carried out in aqueous solution, where acid ⇌ lactone conver-

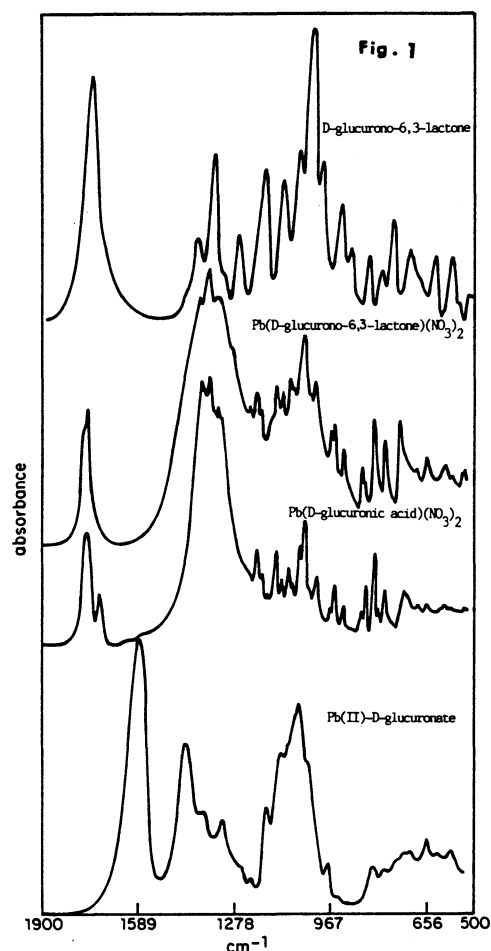


Fig. 1. The FT-IR spectra of D-glucurono-6,3-lactone and its lead(II) complexes in the region of 1900—500 cm^{-1} .

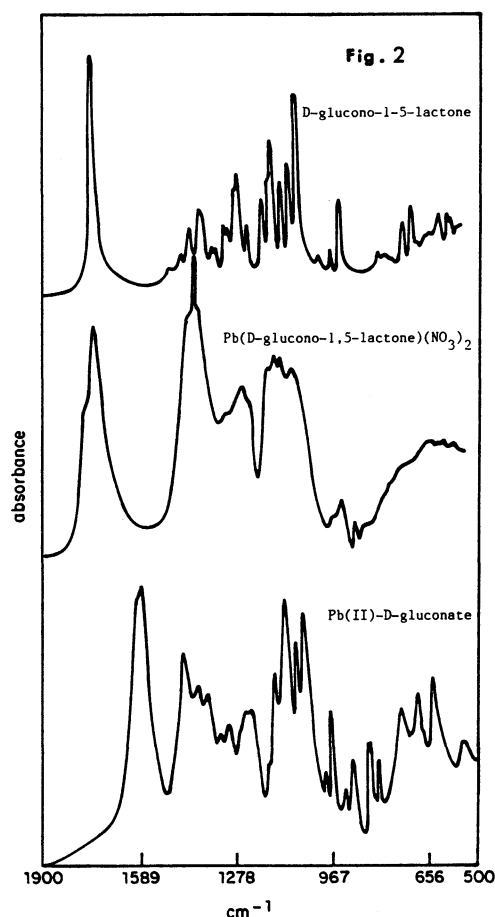


Fig. 2. The FT-IR spectra of D-glucono-1,5-lactone and its lead(II) complexes in the region of 1900—500 cm^{-1} .

sion is readily occurred). Since the separation between the two components of the C=O groups in the Pb-acid ($\Delta\bar{\nu}=28\text{ cm}^{-1}$) and Pb-lactone adducts ($\Delta\bar{\nu}=3\text{ cm}^{-1}$) are different, therefore, the spectral changes observed for the carbonyl groups are related to two different metal-sugar complexes. On the other hand, even an absorption band is present at about 1758 cm^{-1} , both in the free lactone and the Pb-acid adduct, the one at 1758 cm^{-1} in the free lactone has lost most of its intensity in the spectrum of the Pb-acid adduct (Fig. 1) and this is indicative of the complexed C=O group and it is not related to the free lactone (present in the lead-acid compound). However, the purity of these Pb-sugar adducts are also confirmed from their ^{13}C NMR spectra (see next pages). On comparing the IR spectra of the Pb-sugar adducts with that of the Pb(II)-D-glucuronate (Fig. 1), one can see that the carbonyl stretching vibration of the free acid at 1709 cm^{-1} , shifted towards lower frequencies and split into two components at 1583 and 1420 cm^{-1} , in the spectrum of the lead-D-glucuronate. These two absorption bands are related to the anti-symmetric and symmetric OCO^- stretching vibrations.^{11,12} The observed spectral changes for the carboxylate group, in the spectrum of the lead-D-

glucuronate are due to the ionization and the participation of the sugar OCO^- group in metal-ligand bonding.

D-Glucono-1,5-lactone. The C=O stretching vibration of the free D-glucono-1,5-lactone was observed as a strong band at 1728 cm^{-1} and exhibited shifting and splitting at 1775 and 1741 cm^{-1} , in the spectrum of the Pb(D-glucono-1,5-lactone)(NO_3)₂ adduct (Fig. 2). The shifting and splitting of the carbonyl stretching vibration is indicative of the Pb-sugar binding through the lactone carbonyl oxygen atom. Similar changes were observed for the C=O group in the Ag(D-glucono-1,5-lactone) NO_3 adduct, where the silver sugar binding was suggested to be through carbonyl oxygen atom.⁹ On the other hand, in the IR spectrum of the Pb(II)-D-gluconate, the carbonyl stretching vibration showed splitting and shifting towards lower frequency (Fig. 2). The two broad and strong bands at 1586 and 1430 cm^{-1} in the spectrum of the lead-gluconate are attributed to the anti-symmetric and symmetric OCO^- stretching vibrations.⁹ It should be noted that, in the crystal structure of the Pb(II)-D-gluconate,¹⁶ the Pb(II) ion was bonded to four D-gluconate residues through a carboxylato oxygen atom and an OH group (in α -

position) of the two sugar anions (chelation) and to a carboxylato oxygen atom of the other two sugar anions (unidentately). It is worth mentioning that, no Pb-sugar containing bonded D-glucuronic acid can be isolated, due to the partial acid ionization and salt formation and this is evident, by the presence of a strong band at about 1600 cm^{-1} , which is related to the antisymmetric sugar OCO^- stretching vibration.⁹⁾

Other sugar absorption bands in the region of $1350\text{--}900\text{ cm}^{-1}$ related to the strongly coupled OH, CO, and CH modes,^{17,18)} exhibited drastic changes, upon Pb(II) interaction (Figs. 1 and 2). The shifting and intensity changes observed in this region for the OH bending and C-O stretching vibrations are related to the participation of the sugar OH and CO groups in metal sugar bindings.

Nitrato Group Vibrational Frequencies and Binding Modes. The strong and broad absorption band at about 1400 cm^{-1} related to the ν_3 of the ionic nitrate in D_{3h} symmetry,¹⁹⁾ exhibited shifting and splitting in the spectra of the Pb(D-glucurono-6,3-lactone)(NO_3)₂, Pb(D-glucuronic acid)(NO_3)₂, and Pb(D-glucono-1,5-lactone)(NO_3)₂ adducts (Figs. 1 and 2). The splitting of the NO_3^- band at 1380 cm^{-1} is indicative of the presence of the nitrato group in lower symmetry and the possible Pb- NO_3 coordination. Similar changes were observed for the nitrato group vibration in the IR spectra of the Ag(D-glucurono-6,3-lactone) NO_3 , Ag(D-glucuronic acid) NO_3 , and Ag(D-glucono-1,5-lactone)- $\text{NO}_3 \cdot \text{H}_2\text{O}$ adducts,⁹⁻¹²⁾ where the possibility of the bridging NO_3^- group (sugar-Ag- NO_3 -Ag-sugar) and the ionic NO_3^- was proposed. Thus a similar nitrate binding modes (bridging and ionic) could be suggested, in these Pb-sugar adducts. This is also consistent with the molar conductivities observed for the free Pb(NO_3)₂ and its sugar adducts, which indicated the presence of both bonded and ionic NO_3^- groups, in aqueous solutions. Other nitrate absorption bands in the region of $1300\text{--}7000\text{ cm}^{-1}$ were masked by the strong sugar vibrations (Figs. 1 and 2).

Solution Spectra. In D_2O solution, the IR spectra of the free lactones, acids, and their lead(II) complexes in the region of $1900\text{--}1400\text{ cm}^{-1}$, showed marked similarities with those of the corresponding solid compounds. The C=O stretching vibrations of the free lactones at about 1750 cm^{-1} (D-glucurono-6,3-lactone), 1700 cm^{-1} (D-glucuronic acid), and 1720 cm^{-1} (D-glucono-1,5-lactone) showed splitting and shifting towards higher frequencies, in the spectra of the Pb(NO_3)₂-sugar adducts. These changes are consistent with the Pb(II) ion binding to the carbonyl oxygen atoms of the free lactone and acid. On the other hand, in the spectra of the Pb(II)-D-glucuronate and Pb(II)-D-gluconate, the carboxyl stretching vibrations showed splitting and shifting towards lower frequencies, which are characteristic of the acid ionization and salt formation. The observed spectral changes in aqueous solution also indicate the participation of the

sugar C=O group in the Pb-lactone and Pb-acid complexation, while in the Pb-sugar salts the OCO^- is mainly involved in metal-sugar bindings.

^{13}C and ^1H NMR Spectra. The ^{13}C NMR spectra of D-glucurono-6,3-lactone, D-glucuronic acid, D-glucono-1,5-lactone, and D-glucuronic acid have been reported.^{20,21)} In this work, in D_2O solution, the ^{13}C NMR chemical shifts (δ/ppm) were observed for D-glucono-1,5-lactone, 175.20 (C-1), 82.24 (C-2), 75.70 (C-3), 72.00 (C-4), 67.95 (C-5), 60.80 (C-6), for the Pb(D-glucono-1,5-lactone)(NO_3)₂, 177.50 (C-1), 83.20 (C-2), 73.70 (C-3), 72.20 (C-4), 67.90 (C-5), 60.88 (C-6), for D-glucuronic acid, 176.40 (C-1), 73.25 (C-2), 72.30 (C-3), 71.95 (C-4), 71.50 (C-5), 63.50 (C-6), for Pb(II)-D-gluconate, 180.50 (C-1), 75.40 (C-2), 72.99 (C-3), 71.99 (C-4), 71.77 (C-5), 63.40 (C-6), for β -D-glucurono-6,3-lactone, 103.60 (C-1), 74.90 (C-2), 85.60 (C-3), 78.55 (C-4), 70.50 (C-5), 177.50 (C-6), for Pb(D-glucurono-6,3-lactone)(NO_3)₂, 103.7 (C-1), 74.95 (C-2), 85.60 (C-3), 78.60 (C-4), 71.20 (C-5), 178.50 (C-6), for β -D-glucuronic acid, 96.90 (C-1), 74.65 (C-2), 76.35 (C-3), 72.45 (C-4), 75.40 (C-5), 173.40 (C-6), for Pb(D-glucuronic acid)(NO_3)₂, 96.80 (C-1), 74.70 (C-2), 76.40 (C-3), 73.20 (C-4), 75.50 (C-5), 174.50 (C-6), and for Pb(II)-D-glucuronate, 96.85 (C-1), 74.80 (C-2), 76.40 (C-3), 72.90 (C-4), 73.60 (C-5), and 177.40 (C-6). As it is evident, D-glucono-1,5-lactone and D-gluconate anion bind the Pb(II) ion via O-1, and O-2 (due to the downfield shifts of the C-1 and C-2 chemical shifts for both lactone and acid) and this is consistent with the structural analysis of the Pb(II)-D-gluconate, which showed Pb(II) ion binding through O-1 (carboxylato) and O-2 oxygen atoms.¹⁶⁾ Similarly, the major downfield shifts for the C-6 and C-5 chemical shifts of the β -D-glucurono-6,3-lactone, C-6 and C-4 of the β -D-glucuronic acid would indicate the Pb(II) binding via a carbonyl oxygen atom in concert with O(5)-H (lactone) or O(4)-H (acid) (chelation). Similar binding of the D-glucuronate anion was observed in the crystal structure of D-glucuronate- $\text{CaBr} \cdot 3\text{H}_2\text{O}$, with one of the sugar anion being bonded to Ca(II) ion via a OCO^- oxygen and O(4)-H group.¹³⁾

The ^1H NMR spectra of the free D-glucurono-6,3-lactone and D-glucuronic acid in D_2O solution showed both α - and β -anomer forms with the α -H chemical shift at δ 5.56, and β -H at δ 5.45 for the free lactone and α -H at δ 5.58 and β -H at δ 5.28 for the free acid, with the β -anomer domination for both lactone and acid. In the spectra of the Pb(D-glucurono-6,3-lactone)(NO_3)₂ and Pb(D-glucuronic acid)(NO_3)₂ and Pb(II)-D-glucuronate, the β -anomer was found. It has been suggested²²⁾ that the binding modes of the α - and β -anomers of D-glucuronic acid are different and in order one can have a better understanding of the binding modes of D-glucuronate or D-gluconate anion, a comparison between the coordination chemistry of the two acids has been made here.

Coordination Chemistry of D-Glucuronic Acid. Among all the metal D-glucuronate compounds

formed, the crystal structures of potassium-D-glucuronate $\cdot 2\text{H}_2\text{O}$,²³⁾ and D-glucuronate-CaBr $\cdot 3\text{H}_2\text{O}$ ¹³⁾ are known through X-ray diffraction measurements. In the potassium salt, the potassium ion is surrounded by the sugar O-1, O-3, O-6, O-6', and two H_2O molecule, with sugar anion having β -anomer configuration.²³⁾ In the D-glucuronate-CaBr $\cdot 3\text{H}_2\text{O}$, the calcium ion is bonded to three sugar anions, through O-6, O-5 of the first, O-6', O-4 of the second, and O-1, O-2 of the third sugar anion as well as to two H_2O molecule, with sugar having α -anomer form.¹³⁾ As it is evident, the α -anomer complexes via both carboxylate oxygen atoms and in concert with ring O-5 or O(4)-H group (chelation). Recently, on the basis of the ^{13}C NMR spectroscopy,²⁴⁾ and other techniques,²⁵⁾ it has been shown how copper and molybdenum ions bind to D-glucuronate anion, in aqueous solution and the solid state. In the presence of the Cu(II) ion of different concentrations and at variable pH's, the binding modes of D-glucuronic acid have been monitored²⁴⁾ and the flexibility of this sugar moiety towards metal ion coordination has been shown. The main binding sites are the carboxylate oxygen atom (unidentately) or chelation in concert with other sugar OH groups,²⁵⁾ while molybdenum binding was suggested to be through sugar hydroxyl groups as well as the carboxylate anion.²⁵⁾ Therefore, the binding of the Pb(II) ion could be through a carboxylate oxygen atom and O-4 (chelation)(in both acid and anion), while lactone binding is possibly through carbonyl O-6 and O(5)-H group.

Coordination Chemistry of D-Gluconic Acid. The crystal structures of the sodium-D-gluconate,²⁶⁾ potassium-D-gluconate,²⁷⁾ potassium-D-gluconate $\cdot \text{H}_2\text{O}$,²⁸⁾ ammonium-D-gluconate,²⁹⁾ manganese-D-gluconate $\cdot 2\text{H}_2\text{O}$,¹⁴⁾ and lead-D-gluconate¹⁶⁾ are known through X-ray diffraction analysis. The Na^+ ion binds to six oxygen atoms belonging to six different D-gluconate anions with the participation of the OCO^- group and other sugar OH groups (except O-3).²⁶⁾ The K^+ ion in the potassium-D-gluconate is bonded to both carboxylate and OH group oxygen atoms,²⁷⁾ whereas the potassium-D-gluconate $\cdot \text{H}_2\text{O}$ contains two different types of crystals, in which one of the potassium ion is bonded to the sugar OH groups and not the carboxylate group,³⁰⁾ while in the other crystal potassium ion binding is through both sugar OH and OCO^- groups as well as H_2O molecule.²⁸⁾ In the ammonium-D-gluconate, the NH_4^+ has a strong hydrogen bonding network with all the sugar OH groups, which stabilizes the crystal structure.²⁹⁾ In the manganese(II)-D-gluconate $\cdot 2\text{H}_2\text{O}$, the Mn(II) ion is coordinated to two sugar anions through a carboxylate oxygen atom and an OH group of each anion as well as to two H_2O , forming hexa-coordinated metal ion.¹⁴⁾ In the Pb(II)-D-gluconate, the Pb(II) ion is bonded to four sugar anions via a carboxylate oxygen atom and O(2)-H group of the two anions and to a OCO^- oxy-

gen atom of the other two anions, resulting into a hexa-coordinate Pb(II) ion.¹⁶⁾ Therefore, it seems that the main binding of the D-gluconate anion is through carboxylate oxygen atoms and O(2)-H hydroxyl group (in α -position), forming a five-membered ring with metal cations. This is also true for the Pb(II) ion binding here, which is through a carboxylate oxygen atom and O(2)-H group of each D-gluconate anion, while in the Pb-lactone adduct, the binding could be through the C=O oxygen atom and the O(2)-H hydroxyl group.

Conclusion

On the basis of the spectroscopic (FT-IR, ^1H and ^{13}C NMR) and structural properties of the D-glucurono-6,3-lactone, D-glucuronic acid, and D-glucono-1,5-lactone and their Pb(II) complexes, the following points can be emphasized:

(a) In the Pb(D-glucurono-6,3-lactone)(NO_3)₂ adduct, the Pb(II) ion could be coordinated to a lactone molecule via C(6)=O and O(5)-H oxygen atoms as well as to two nitrate groups, while in the Pb(D-glucuronic acid)(NO_3)₂, the lead ion is bonded to an acid molecule, through carbonyl O(6') and O(4)-H as well as to two nitrate groups. In the Pb(II)-D-glucuronate, the metal ion is bonded to carboxylate group (one or both oxygen atom) or a carboxylate oxygen atom and O(4)-H group (chelation) of the two acid anions and to a OCO^- oxygen atom of the other two sugar anions, forming a hexa-coordinated Pb(II) ion (similar to that of the Pb(II)-D-gluconate salt).

(b) In the Pb(D-glucono-1,5-lactone)(NO_3)₂, the metal ion would be bonded to a lactone molecule via C(1)=O and O(2)-H oxygen atoms as well as to two nitrate groups. In the Pb(II)-D-gluconate, the lead ion is hexa-coordinated, binding to four sugar anions through a carboxylate oxygen atom and an O(2)-H group of the two anions and to a OCO^- oxygen atom of the other two D-gluconate anions, which is known through X-ray structural determination.¹⁶⁾

(c) The β -anomer sugar configuration is predominant in the free D-glucurono-6,3-lactone, D-glucuronic acid, and their lead sugar complexes.

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