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Structural Properties of Silver(I) and Mercury(II) Complexes of D-Lactobionate: Self-Assembled Coordination Polymers

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Single crystals of silver(I) and mercury(II) D-lactobionates (LBA) grown from aqueous solutions were subjected to X-ray analysis. Both compounds crystallize in the monoclinic space group *C*2 (No. 5) with unit cell dimensions $a = 29.621(5)$ Å, $b = 7.392(2)$ Å, $c = 7.430(2)$ Å, and $\beta = 90.75(2)°$ for Ag[LBA]·H_2O and $a = 29.084(3)$ Å, $b = 7.4066(11)$ Å, $c = 7.4761(9)$ Å, and $= 90.718(9)°$ for Hg[LBA]$_2$·2H_2O. Final solutions of both crystal structures reveal that both sugar acid−metal complexes form novel metal-bridged polysaccharides having similar structures achieved by coordination of alcoholic oxygens O(3) and O(6′) in LBA to the metals, although both complexes have different local geometries around metal ions: distorted trigonal bipyramidal for Ag[LBA]·H_2O and octahedral for Hg[LBA]$_2$·2H_2O. Intermolecular interactions were observed through hydrogen bondings of O(4′) in the galactosyl unit with O(5) and O(6) in the gluconic acid moieties of the upper polymeric unit, which is presumed to be an important factor inducing the formation of polymeric structures. In addition, a carbohydrate−carbohydrate interaction was also observed through hydrogen bondings between O(2′) and O(3′) of neighboring galactosyl units. Silver(I) and mercury(II) complexes lose their polymeric nature in water in different manners: the silver(I) complex is fully dissociated, but the mercury(II) complex exists as a monomeric neutral form.

Introduction

The interaction of sugar acids with various metal ions has attracted a great deal of attention in recent years[1] because of the importance of these in biological systems[2] and potential use as sequestering agents related to environmental and toxicological problems[3] as well as potential medical applications.[4,5] Sugar acids such as D,L-gluconic acid and lactobionic acid play an important role in carbohydrate metabolism.[6] Lactobionic acid is a natural disaccharide composed of galactose and gluconic acid connected by a glycosidic linkage and obtained from stoichiometric oxidation of the disaccharide by *Pseudomonas graveolens*.[7] Such sugar acids containing both carboxylate and hydroxyl groups are expected to chelate metal ions via various different bonding modes depending on the metal ions and reaction conditions. Structural properties of the complexes between the sugar acids and metal ions are very important for practical applications and therefore have been extensively studied in solution using various spectroscopic and electrochemical methods.[1] However, only a few X-ray structures[8] have been reported for the isolated metal complexes of these sugar acids.

We have successfully obtained good single crystals of silver(I) and mercury(II) complexes of D-lactobionate (4-*O*-β-D-galactopyranosyl-D-gluconate: LBA) from their aqueous solutions, which have been found in this study to be, in the solid state, coordination polymers self-assembled by hydrogen-bonding interactions between sugar acids. Here we report the detailed structural aspects of silver(I) and mercury(II) complexes of LBA and their behaviors in aqueous solution as well as their thermal properties.

Experimental Section

Materials and Instrumentation. Silver(I) nitrate, mercury(II) chloride, and lactose purchased from Aldrich were used as received. The potassium salt of lactobionate was prepared by oxidation of lactose following the literature method.[9]

Elemental analyses, TGA, and DSC were performed at the Advanced Analysis Center of KIST. Freezing point depression and conductance were measured using a Precision Systems model 5002 osmometer and a YSI model 32 conductometer, respectively. ^1H and ^{13}C NMR spectra were recorded in D_2O solutions on a Varian Gemini-300 NMR spectrometer operating at 300 and 75 MHz, respectively, at 298 K. ^1H NMR spectra were referenced to the solvent peak, and ^{13}C NMR spectra were referenced to external $CDCl_3$. Infrared spectra were measured as KBr pellets on an MIDAC model 101025 FT-IR spectrometer.

Preparation of Ag[LBA]·H_2O. Silver(I) nitrate (1.69 g, 10.0 mmol) was added to an aqueous solution (20 mL) of K[LBA] (3.97 g, 10.0

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mmol). Colorless parallelepiped crystals of Ag[LBA]·H_2O began to grow in a few hours. One week later, 4.03 g of the crystals was collected (yield 83.5%); mp 162 °C dec. Anal. Calcd for $AgC_{12}H_{21}O_{12}$·H_2O: C, 29.8; H, 4.80; Ag, 22.3. Found: C, 30.0; H, 4.77; Ag, 22.1. IR (cm^{-1}): 3422 (vs), 2936 (w), 1600 (s), 1404 (m), 1080 (s). ^1H NMR (δ, ppm): 4.59 (d, 1H), 4.21 (s, 1H), 4.13 (s, 1H), 3.60−4.02 (m, 9H). ^{13}C NMR (δ, ppm): 178.63, 103.78, 72.81, 72.56, 72.00, 71.81, 71.36, 68.90, 62.18, 61.31. Molar conductivity of an aqueous solution (11.0 mmol/L) at 26.0 °C (Λ, Ω^{-1} cm^2 mol^{-1}): 78.5. Freezing point depression of the aqueous solution (11.0 mmol/L): 0.038 °C.

Preparation of Hg[LBA]$_2$·2H_2O. Ag[LBA]·H_2O(2.42 g, 5.0 mmol) was reacted with $HgCl_2$ (0.68 g, 2.5 mmol) in aqueous solution (20 mL) for 1 h, and the resultant precipitate (AgCl) was filtered out. The filtrate was slowly concentrated, and 1.70 g of colorless parallelepiped crystals was collected (yield 72.0%). Anal. Calcd for $HgC_{24}H_{42}O_{24}$: 2H_2O: C, 30.3; H, 4.87; Hg, 21.1. Found: C, 30.3; H, 4.83; Hg, 20.9. IR (cm^{-1}): 3448 (vs), 2936 (w), 1622 (s), 1384 (m), 1080 (s). ^1H NMR (δ, ppm): 4.60 (d, 1H), 4.26 (s, 1H), 4.08 (t, 1H), 3.58−4.00 (m, 9H). ^{13}C NMR (δ, ppm): 176.99, 103.63, 80.98, 75.55, 72.77, 72.72, 71.70, 71.60, 71.29, 68.86, 62.19, 61.26. Molar conductivity of an aqueous solution (9.95 mmol/L) at 26.0 °C (Λ, Ω^{-1} cm^2 mol^{-1}): 23.0. Freezing point depression of the aqueous solution (9.95 mmol/L): 0.018 °C.

Crystal Structure Determinations and Refinements. All the X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell dimensions were determined from 25 machine-centered reflections. Intensities of three check reflections monitored every 1 h during the data collection period indicated no significant degradation. Absorption corrections were applied by an empirical ψ-scan method. The Patterson method was employed to locate heavy atoms (SHELXS-86[10a]), and the subsequent cycle of the Fourier map and least-squares refinements located other atoms (SHELXL93[10b]). All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbons were included in the structure factor calculation using a riding model.

Results and Discussion

Syntheses and Structures. Addition of silver(I) nitrate to the aqueous solution of K[LBA] resulted in good single crystals of Ag[LBA]·H_2O. Single crystals of Hg[LBA]$_2$·2H_2O were obtained by the metathesis reaction of Ag[LBA]·H_2O with $HgCl_2$ in aqueous solution followed by slow evaporation of the solvent after removing the precipitate AgCl. Both crystals are fairly stable in the air.

Crystal data for both complexes are summarized in Table 1. Unit cell dimensions of both compounds are intriguingly similar, indicating that their crystal structures are similar. In fact, final solutions of their crystal structures revealed unique similar polymeric natures.

Table 1. Crystallographic Data for Ag[LBA]·H_2O and Hg[LBA]$_2$·2H_2O

	Ag[LBA]·H_2O	Hg[LBA]$_2$·2H_2O
empirical formula	$C_{12}H_{21}O_{12}Ag$·H_2O	$C_{24}H_{42}O_{24}Hg$·2H_2O
fw	483.17	951.20
temp, K	293(2)	293(2)
wavelength, Å	0.710 73	0.710 73
crystal system	monoclinic	monoclinic
space group	*C*2 (No. 5)	*C*2 (No. 5)
a, Å	29.621(5)	29.084(3)
b, Å	7.392(2)	7.4066(11)
c, Å	7.430(2)	7.4761(9)
β, deg	90.75(2)	90.718(9)
V, Å^3	1626.6(6)	1610.3(6)
Z	4	2
crystal color	colorless	colorless
d_{calcd}, g/cm^3	1.973	1.962
μ, mm^{-1}	1.312	4.887
θ range, deg	1.38−24.97	1.40−26.01
no. of reflns obsd	1501	1545
no. of indep reflns [$I > 2\sigma(I)$]	1473	1510
data-to-parameter ratio	1473/235	1510/231
GOF on F^2	1.126	1.074
final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0296$ w$R_2 = 0.0872$	$R_1 = 0.0268$ w$R_2 = 0.0716$

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. w$R_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

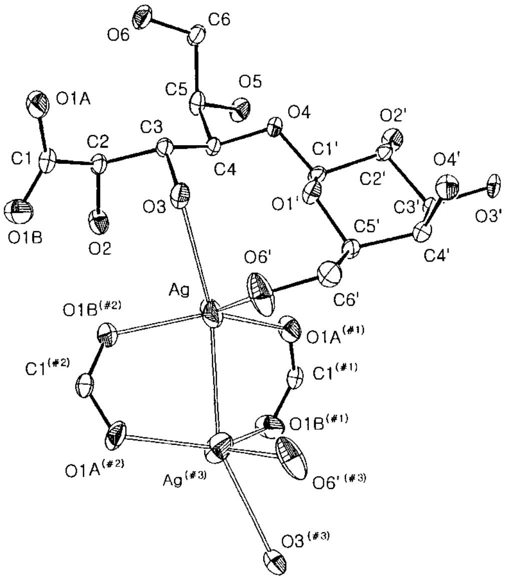

Figure 1. ORTEP drawing of atoms in the asymmetric unit of polymeric Ag[LBA]·H_2O, including neighboring atoms around a silver atom, with atomic labeling scheme. Symmetry relations: (#1) $x, y, 1 + z$; (#2) $1 - x, y, 1 - z$; (#3) $1 - x, y, 2 - z$.

(a) Crystal Structure of Ag[LBA]·H_2O. Figure 1 shows an ORTEP drawing of atoms in the asymmetric unit, including other neighboring atoms around a silver atom, with an atomic labeling scheme. Selected bond distances and angles are listed in Table 2. It is seen from the coordination sphere around Ag atoms in the figure that there is a C_2 axis crossing the center of the line connecting two silver atoms. The local geometry around each silver atom is a distorted trigonal bipyramid with O(3) and the other silver atom at axial positions, which reflect the coordination flexibility of a silver atom. The Ag−Ag distance is 2.8472(11) Å, which is similar to that found in metallic silver (2.89 Å)[11] and also those found in silver(I) complexes of perfluorobutyrate,[12] glycylglycine,[13] trifluoroacetate,[14] and 3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanecarboxylate.[15] The angle O(1A)$^{\#1}$−Ag−O(1B)$^{\#2}$ is 135.1(2)°, which is more folded than those found in (glycylglycine)silver(I) nitrate (160°)[13] and the silver(I) trifluoroacetate complex (157.9(2)°).[14] The Ag−O(1A)$^{\#1}$ and Ag−O(1B)$^{\#2}$ distances are 2.235(4) and 2.227(4) Å, respectively, which are in the range of those of other silver carboxylate complexes. The distances of two alcoholic oxygens, O(6′) and O(3), from silver are 2.456(6) and 2.642(4) Å, respectively, which are much shorter than the sum of van der

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ag[LBA]·H_2O[a]

Distances			
Ag−O(1A)$^{\#1}$	2.235(4)	Ag−O(1B)$^{\#2}$	2.227(4)
Ag−O(6′)	2.456(6)	Ag−O(3)	2.642(4)
Ag−Ag$^{\#3}$	2.8472(11)	O(1A)−C(1)	1.248(7)
O(1B)−C(1)	1.233(7)		
Angles			
O(1A)$^{\#1}$−Ag−O(1B)$^{\#2}$	135.1(2)	O(1A)$^{\#1}$−Ag−O(6′)	107.9(2)
O(1B)$^{\#2}$−Ag−O(6′)	114.1(2)	O(1A)$^{\#1}$−Ag−Ag$^{\#3}$	80.15(11)
O(1B)$^{\#2}$−Ag−Ag$^{\#3}$	80.94(11)	O(6′)−Ag−Ag$^{\#3}$	95.16(13)
C(6′)−O(6′)−Ag	124.7(4)	O(1B)−C(1)−O(1A)	127.3(5)
Intermolecular Hydrogen Bonds			
O(2′)−O(3′)$^{\#4}$	2.687(5)	O(2′−O(5)$^{\#5}$	2.940(5)
O(2′)−O(6)$^{\#1}$	2.714(6)	O(3′)−O(5)$^{\#5}$	2.737(5)
O(4′)−O(5)$^{\#6}$	2.757(5)	O(4′)−O(6)$^{\#7}$	2.748(6)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $x, y, z + 1$; (#2) $-x + 1, y, -z + 1$; (#3) $-x + 1, y, -z + 2$; (#4) $-x + 0.5, y + 0.5, -z + 2$; (#5) $-x + 0.5, y - 0.5, -z + 2$; (#6) $x, y - 1, z$; (#7) $x, y - 1, z + 1$.

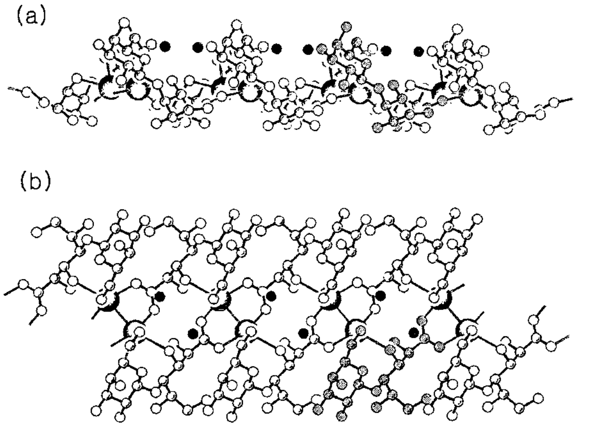


Figure 2. PLUTON diagrams of a polymeric chain of Ag[LBA]·H_2O: (a) upper view of the polymeric chain (viewed along the *a* axis); (b) side view of the polymeric chain (viewed along the *b* axis). Hydrogens are omitted for clarity. Black circles are water molecules. One lactobionate molecule is shaded.

Waals radii (3.2 Å)[16] of silver and oxygen atoms. The interactions of metal ions with hydroxyl groups in the sugar acids were indeed predicted on the basis of NMR and IR spectroscopic data from other work.[1c,d,f] The coordination of alcoholic oxygen to a silver atom was also found in a poorly characterized silver complex of 3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanecarboxylate where the Ag−O distance was found to be 2.46 Å.[15]

The polymeric feature of the complex is shown in Figure 2. Two lactobionate molecules are linked as a dimeric unit by two silver atoms bridged by carboxylate groups. A unique polymeric nature of the complex is achieved by the coordination of alcoholic O(3) and O(6′) atoms to another silver atom. A polymeric unit of Ag[LBA]·H_2O shows a grating-like structure with double arrays of sugar rings. The side view of the polymer reveals the structure of a sigmoid curve with a pitch of 7.430(2) Å. The interior between neighboring sugar rings can be regarded as a major groove, and a niche site at the bottom of the polymeric unit will be called a minor groove for convenience. One major groove confines two water molecules which strongly interact with hydroxyl groups of sugar rings by hydrogen bondings.

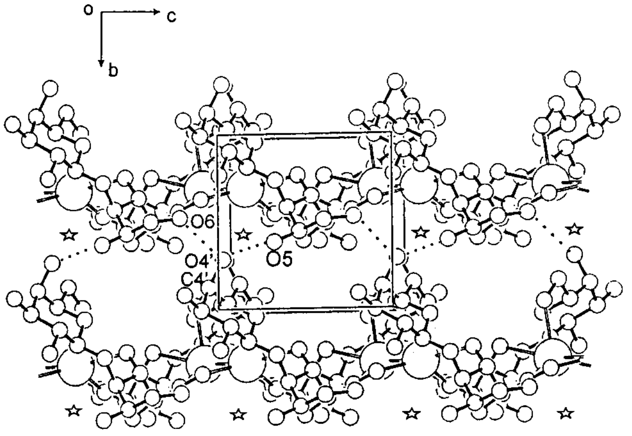
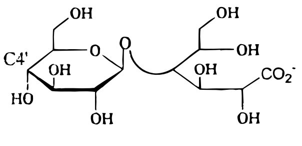


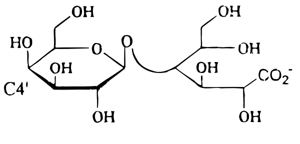
Figure 3. Packing array of polymeric chains of Ag[LBA]·H_2O viewed along the *a* axis. Intermolecular hydrogen bondings (dotted lines) present in the star-marked regions are affected by the configuration of the C(4′) carbon and play an important role in molecular association.

Each Ag[LBA]·H_2O polymer unit interacts compactly with other neighboring units through hydrogen bondings between hydroxyl groups of lactobionates. Figure 3 shows the packing array of polymeric units viewed along the *c* axis. Each polymeric unit is stacked in a constant direction so as to superimpose, presumably, most efficiently the sigmoid curve. An O(4′) atom in a six-membered sugar ring participates in strong hydrogen-bonding interactions with O(5) and O(6) atoms in a minor groove of an upper polymeric unit. The intermolecular distances of O(4′)···O(5) and O(4′)···O(6) are 2.757(5) and 2.748(6) Å, respectively. The regions which show these interactions are marked with stars in Figure 3. The gluconate moieties of lactobionate which consist of summits of the bottom site of a polymeric unit in Figure 3 function as caps on the aforementioned major grooves of the next layer polymeric unit by these hydrogen bondings, and the grooves, consequently, become capsules confining water molecules. The chemistry of self-assembling capsules is currently an important issue.[17] Though the capsules present in our polymers exist only in the solid state, they can be a structural model for the design of novel hydrophilic capsules.

We also attempted to prepare silver(I) complexes of other sugar acids resembling D-lactobionate in structure, but we could not obtain solid products of definite compositions. For example, addition of silver nitrate to an aqueous solution of potassium cellobionate, which is different from the lactobionate only at the configuration of the C(4′) carbon, resulted in a rapid color change of the solution from colorless to dark brown, yielding a mixed precipitate of the same color including a colloidal silver which could not be characterized, presumably due to decomposition. Such a difference is probably ascribed to the different configuration of the C(4′) carbon, and as was mentioned above, the O(4′) atom in the silver(I) lactobionate seems to play an important role in the interaction between a sugar ring and the minor groove of its upper polymeric unit. This interaction



D-Cellobionate



D-Lactobionate

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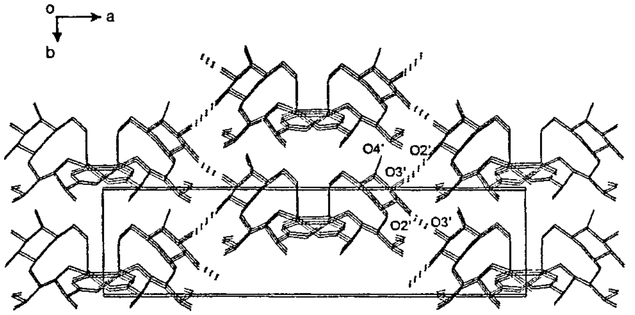

Figure 4. Packing array of polymeric chains of Ag[LBA]$\cdot$H$_2$O viewed along the *c* axis, showing hydrogen bonding interactions (dotted lines) between sugar rings.

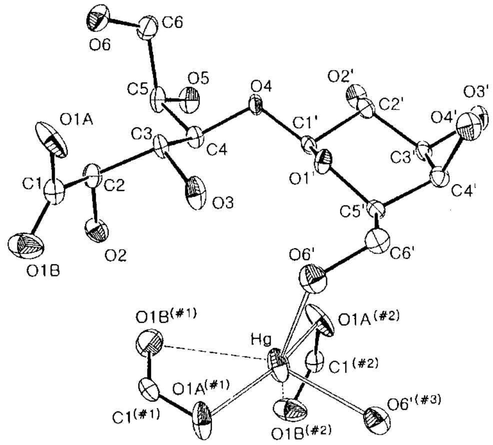

Figure 5. ORTEP drawing of atoms in the asymmetric unit of polymeric Hg[LBA]$_2\cdot$2H$_2$O, including the neighboring atoms around the mercury atom, with atomic labeling scheme. Symmetry relations: (#1) $-x, y, 1 - z$; (#2) $x, y, 1 + z$; (#3) $-x, y, 2 - z$.

present in the star-marked regions of Figure 3 is not possible in the case of silver(I) cellobionate if it is assumed to have the same polymeric structures as silver(I) lactobionate. This is a good example in which the configuration of carbon in the sugar ring plays an important role in molecular association.

Figure 4 is a packing diagram in stick bond style viewed along the *a* axis, which shows carbohydrate–carbohydrate interactions present in Ag[LBA]$\cdot$H$_2$O. The O(2′) and O(3′) atoms in the six-membered sugar ring interact with neighboring O(3′) and O(2′), respectively, by strong hydrogen bonding (the O(2′)$\cdots$O(3′) distance is 2.687(5) Å) in a zigzag manner.

(b) Crystal Structure of Hg[LBA]$_2\cdot$2H$_2$O. Figure 5 depicts an ORTEP drawing of atoms in the asymmetric unit including other atoms around a mercury atom with an atomic labeling scheme. Selected bond distances and angles are listed in Table 3. As shown in Figure 6, Hg[LBA]$_2\cdot$2H$_2$O shows also the grating-like polymeric structure similar to Ag[LBA]$\cdot$H$_2$O. The array of sugar rings is almost the same and each major groove in Hg[LBA]$_2\cdot$2H$_2$O also contains two water molecules.

However, the coordination sphere around the mercury(II) atom is different from that of Ag[LBA]$\cdot$H$_2$O. The coordination geometry around the mercury atom is a distorted octahedron with a C_2 axis crossing the mercury atom and the center of O(6′) and O(6′)$^{\#3}$. The two planes composed of each of the two carboxylate groups and the mercury atom intersect each other perpendicularly. This orientation of carboxylate groups in Hg[LBA]$_2\cdot$2H$_2$O is different from those of other known mercury(II) carboxylate complexes such as phenylmercury(II)[18] acetate and (1,4-dioxane)mercury(II) trifluoroacetate.[19] The distance of the mercury atom to the coordinated carboxylate oxygen O(1A) is 2.134(6) Å, which is a little shorter than those of Ag–carboxylate oxygen bonds. Another carboxylate oxygen, O(1B), interacts weakly with the mercury atom (Hg$\cdots$O(1B): 2.713(6) Å). This kind of asymmetric coordination of carboxylate groups to the mercury(II) was also found in the other mercury(II) complexes.[18,19] The alcoholic O(6′) atom coordinates to Hg with a distance of 2.472(6) Å, which is similar to the corresponding distance in the silver complex. However, unlike that in the Ag(I) complex, the alcoholic O(3) atom does not interact with Hg (Hg$\cdots$O(3): 3.952(5) Å). Such a difference seems to cause a large dihedral angle of C(5′)–C(6′)–O(6′)–Hg (57.7(7)°) compared with that of C(5′)–C(6′)–O(6′)–Ag (17.2(7)°), although the angles C(6′)–O(6′)–Hg (125.5(4)°) and C(6′)–O(6′)–Ag (124.7(4)°) are similar.

Crystal packing also exhibits capsules and carbohydrate–carbohydrate interactions similar to those in Ag[LBA]$\cdot$H$_2$O, which is not displayed in this paper. The fact that the two complexes have similar polymeric structures and stacking

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Hg[LBA]$_2\cdot$2H$_2$O[a]

Distances			
Hg–O(1A)$^{\#1}$	2.134(6)	Hg–O(1B)$^{\#1}$	2.713(6)
Hg–O(6′)	2.472(6)	O(1A)–C(1)	1.290(9)
O(1B)–C(1)	1.213(10)		
Angles			
O(1A)$^{\#1}$–Hg–O(1A)$^{\#2}$	154.7(3)	O(1A)$^{\#1}$–Hg–O(1B)$^{\#2}$	108.7(2)
O(1A)$^{\#1}$–Hg–O(1B)$^{\#1}$	52.6(2)	O(1B)$^{\#1}$–Hg–O(6′)	99.3(2)
O(1B)$^{\#1}$–Hg–O(1B)$^{\#2}$	98.1(3)	O(1B)$^{\#1}$–Hg–O(6′)$^{\#3}$	149.1(2)
O(1A)$^{\#1}$–Hg–O(6′)$^{\#3}$	97.4(2)	O(1A)$^{\#2}$–Hg–O(6′)$^{\#3}$	102.2(2)
O(6′)$^{\#3}$–Hg–O(6′)	77.8(3)	C(6′)–O(6′)–Hg	125.5(4)
O(1B)–C(1)–O(1A)	124.0(7)		
Intermolecular Hydrogen Bonds			
O(2′)–O(3′)$^{\#4}$	2.687(9)	O(2′)–O(5)$^{\#5}$	2.934(7)
O(2′)–O(6)$^{\#2}$	2.737(10)	O(3′)–O(5)$^{\#5}$	2.745(5)
O(4′)–O(5)$^{\#6}$	2.794(7)	O(4′)–O(6)$^{\#7}$	2.783(8)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x, y, 1 - z$; (#2) $x, y, 1 + z$; (#3) $-x, y, 2 - z$; (#4) $-x + 0.5, y - 0.5, -z + 2$; (#5) $-x + 0.5, y + 0.5, -z + 2$; (#6) $x, y + 1, z$; (#7) $x, y + 1, z + 1$.

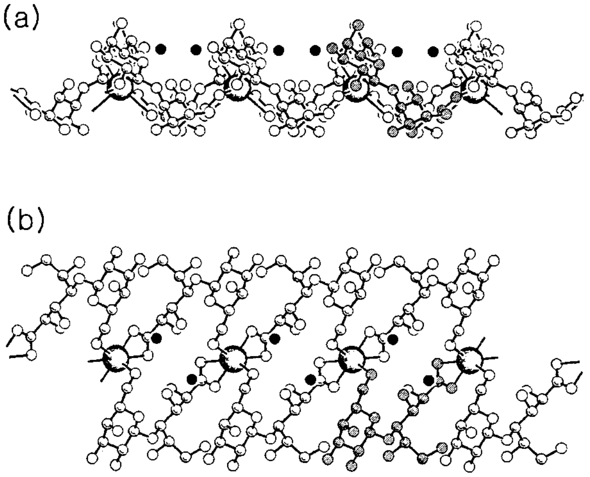

Figure 6. PLUTON diagrams of a polymeric chain of Hg[LBA]$_2\cdot$2H$_2$O: (a) upper view of the polymeric chain (viewed along the *b* axis); (b) side view of the polymeric chain (viewed along the *a* axis). Hydrogens are omitted for clarity. Black circles are water molecules. One lactobionate molecule is shaded.

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Table 4. ^{13}C NMR Data for Metal Lactobionates[a]

	δ, ppm		
carbon	K[LBA]	Ag[LBA]	Hg[LBA]$_2$
C(1)	178.8	178.6	177.0
C(4)	81.9	81.8	80.9
C(6)	61.3	61.3	61.3
C(1′)	103.8	103.8	103.6
C(4′)	68.9	68.9	68.9
C(5′)	75.6	75.5	75.6
C(6′)	62.2	62.2	62.2

[a] Chemical shift assignments were determined by comparison with those of other compounds reported in the literature.[7] Chemical shifts of other carbons appear in the range 71−73 ppm.

features despite different coordination properties of the two metal ions implies that the sugar acid−sugar acid interactions are more important driving forces in the formation of polymeric complexes than the local geometry around the metal ions.

Solution Behaviors. The lactobionate complexes of silver(I) and mercury(II) are marginally soluble in water at room temperature but become very soluble above 60 °C. Both complexes are stable in water and in the air, which is rather contrary to the conception that silver and mercury carboxylates are unstable.

Table 4 lists the data for the chemical shift assignments of ^{13}C NMR spectra of K[LBA], Ag[LBA], and Hg[LBA]$_2$. ^{13}C NMR spectra of K[LBA] and Ag[LBA] exhibit the same patterns with almost the same chemical shifts. The Ag[LBA] complex is, hence, considered to be fully dissociated in water in the same way as K[LBA]. Such a result could be confirmed by both molar conductivity data at 26.0 °C (78.5 Ω^{-1} cm^2/mol) and freezing point depression data (11.0 mmol solution of Ag[LBA] depressed freezing point corresponding to 22.0 mmol of a neutral molecule).

Solution behavior of Hg[LBA]$_2$ is, however, remarkably different from that of Ag[LBA]. The C(1) carbon resonance in the ^{13}C NMR spectrum appears at 177.0 ppm which is shifted upfield from that of K[LBA] by 1.6 ppm. The identical C(6′) chemical shifts for Ag[LBA] and Hg[LBA]$_2$ indicate that the alcoholic O(6′) dissociates from mercury in solution. The molar conductivity of Hg[LBA]$_2$ at 26.0 °C is 23.0 Ω^{-1} cm^2/mol, which falls in the range of a nonelectrolyte. A freezing point depression study with 9.95 mmol equiv of Hg[LBA]$_2$ also indicates that this complex is a nondissociated monomeric complex. From these results, it can be concluded that the mercury(II) complex of LBA exists in water as a monomeric neutral complex with Hg−carboxylate bonds retained. Different properties for silver(I) and mercury(II) complexes of LBA in aqueous solution seem to be ascribed to different coordination properties of the metal ions.

Thermal Properties. Figure 7a displays TGA curves for both complexes, and Figure 7b displays DSC results for Ag[LBA]·H$_2$O only. Diminution of weight by 2.65% observed in the TGA curve for Ag[LBA]·H$_2$O in the temperature range of 80−140 °C is an indication of the loss of water molecules confined in the grooves. Energy absorbed by water molecules during the loss was calculated from the integration of the DSC curve, and its value corresponds to 5.2 kcal/mol, which falls in the range expected for energy of water dimerization[20] and so is assumed to be the hydrogen-bonding energy of water molecules in capsules. Ag[LBA]·H$_2$O began to decompose, exhibiting a dark color, above 160 °C, presumably due to the catalytic activity of the silver ion.

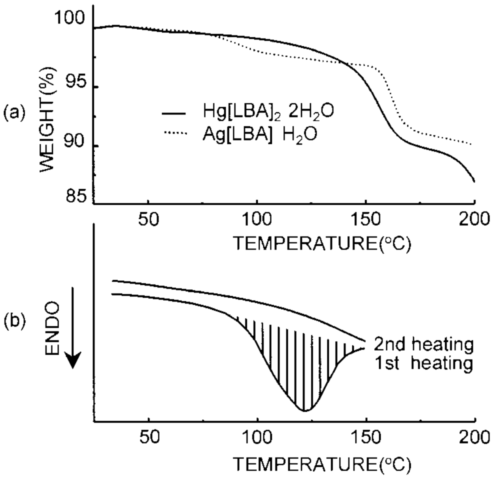

Figure 7. (a) TGA diagrams for Ag[LBA]·H$_2$O (dotted line) and Hg[LBA]$_2$·2H$_2$O (solid line); (b) DSC diagram of Ag[LBA]·H$_2$O.

Table 5. Close Distances from a Water Molecule to Neighboring Atoms

	O$_w$···A, Å	
A	Ag[LBA]·H$_2$O	Hg[LBA]$_2$·2H$_2$O
O(2)	2.84	2.76
O(3)	3.01	2.87
O(6′)	2.75	2.64
metal	4.02	3.74

Hg[LBA]$_2$·2H$_2$O does not lose weight up to 150 °C, in contrast with Ag[LBA]·H$_2$O, and begins to decompose above 160 °C like Ag[LBA]·H$_2$O. A water molecule in both metal complexes is strongly hydrogen-bonded to neighboring hydroxyl groups as shown in Table 5. However, a water molecule in Hg[LBA]$_2$·2H$_2$O more closely interacts with neighboring metal and hydroxyl groups, which is presumably the reason for the stronger stability of confined water molecules in the groove of Hg[LBA]$_2$·2H$_2$O to external heat.

Conclusions. We have examined the crystal structures of silver(I) and mercury(II) complexes of LBA in order to elucidate intra- and intermolecular interactions of the metal-bridged polysaccharides in the solid state. The solid state silver(I) and mercury(II) complexes of LBA are assembled by specific hydrogen-bonding interactions between lactobionate molecules. Silver(I) and mercury(II) complexes lose their polymeric nature in water in different manners: the silver(I) complex is fully dissociated, but the mercury(II) complex exists as a monomeric neutral form.

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Supporting Information Available: Listings of detailed crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters for non-hydrogen atoms, and atomic coordinates and isotropic displacement parameters for hydrogen atoms (9 pages). X-ray crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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