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Preparation, Spectroscopic and Structural Analysis of Uranium-Arabinose Complexes

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The reaction between *L*-arabinose and hydrated uranyl salts has been investigated in aqueous solution and the solid complexes of the type $UO_2(L$-arabinose$)X_2 \cdot 2 H_2O$, where $X = Cl^-$, Br^-, and NO_3^-, have been isolated and characterized. Due to the marked similarities with those of the structurally known Ca(*L*-arabinose)$X_2 \cdot 4 H_2O$ and Mg(*L*-arabinose)$X_2 \cdot 4 H_2O$ ($X = Cl^-$ or Br^-) compounds, the UO_2^{2+} ion binds obviously to two *L*-arabinose moieties, through O1, O5 of the first and O3, O4 of the second molecule resulting into a six-coordinated geometry around the uranium ion with no direct U—*X* ($X = Cl^-$, Br^- or NO_3^-) interaction. The intermolecular hydrogen bonding network of the free *L*-arabinose is rearranged upon uranium interaction. The β-anomer configuration is predominant in the free *L*-arabinose, whereas the α-anomer conformation is preferred in the uranium complexes.

(Keywords: Sugars; Uranium-arabinose; Arabinose complexes)

Darstellung, spektroskopische und Strukturanalyse von Uran-Arabinose Komplexen

Es wurde die Reaktion zwischen *L*-Arabinose und hydratisierten Uranylsalzen in wäßriger Lösung untersucht und kristalline Komplexe des Typs $UO_2(L$-Arabinose$)X_2 \cdot 2 H_2O$ mit $X = Cl^-$, Br^- und NO_3^- isoliert und charakterisiert. Wie aus markanten Ähnlichkeiten der Komplexe mit den bekannten Verbindungen Ca(*L*-Arabinose)$X_2 \cdot 4 H_2O$ und Mg(*L*-Arabinose)$X_2 \cdot 4 H_2O$ ($X = Cl^-$ oder Br^-) abzuleiten ist, bindet das UO_2^{2+}-Ion mit zwei *L*-Arabinose Einheiten, wobei sich durch die O1,O5-Koordination des ersten und die O3,O4-Koordination des zweiten Moleküls eine sechs-koordinierte Geometrie um das Uranylion [ohne direkte U—*X* ($X = Cl^-$, Br^- oder NO_3^-) Wechselwirkung] ausbildet. Die intermolekularen Wasserstoffbrücken zeigen nach der Wechselwirkung mit dem Uranylion eine Umgruppierung. In der freien *L*-Arabinose ist das β-Anomere vorherrschend, in den Urankomplexen hingegen das α-Anomere.

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Introduction

In our previous communication [1], we have reported the interaction of *D*-glucuronic acid with hydrated uranyl salts. The UO_2^{2+} ion favoured the *β*-anomer configuration of this sugar moiety, whereas the alkaline earth metal cations preferred the *α*-anomer complexation [2]. The alkali [3], alkaline earth [4, 5] and the zinc group [6] metal ions preferred the *α*-anomer configuration of the *L*-arabinose molecule. In the present work, we describe the synthesis and characterization of several uranyl-arabinose complexes in solid and in solution using FT-IR, proton-NMR spectroscopy, molar conductivity and X-ray powder diffraction techniques that have not been reported so far. On the other hand, the spectroscopic properties of these metal-*L*-arabinose complexes are compared with those of the corresponding structurally characterized Ca(II), Mg(II) and the zinc group metal ions [4–6]. This comparison allowed us to draw conclusions concerning the characteristic features of each structural type of compounds for the uranium ion and to establish a correlation between the spectral changes and the binding sites of the *L*-arabinose molecule. Furthermore, the effect of metal coordination on the configurational changes in the ligand is discussed and possible assignments for the sugar vibrational frequencies are reported, based on the X-ray and neutron structural analyses reported in the literature [7, 8].

Experimental

Hydrated uranyl nitrate and uranyl chloride were BDH reagent grade and used as supplied. Hydrated uranyl bromide salt was prepared according to our previous report [9] by metathesis of $UO_2(NO_3)_2$ with $BaBr_2$ in methanol and filtering off the insoluble $Ba(NO_3)_2$. *L*-arabinose was BDH and recrystallized from water. All the other chemicals were reagent grade and used as supplied.

Preparation of the Complexes. Hydrated uranyl salts (1 mmol) in methanol (20 ml) was added to a hot solution of *L*-arabinose (1 mmol) in methanol (20 ml). After heating the solution for 30 min at 80 °C the solution was cooled down to room temperature and left for a period of one week. The pale yellow crystalline compounds that precipitated were filtered off and washed with methanol several times and dried over $CaCl_2$. The analytical results showed the composition of $UO_2(L\text{-arabinose})X_2 \cdot 2\,H_2O$ ($X = Cl^-$, Br^- and NO_3^-). The uranyl-sugar compounds are very soluble in water and alcohol, but not soluble in any other common organic solvents. The compounds are hygroscopic and should be kept in a desiccator.

Physical Measurements. Infrared spectra were recorded on a DIGILAB FTS 15/C Fourier Transform Michelson Infrared Interferometer, equipped with a high sensitivity HgCdTe detector and a KBr beam splitter, with a spectral resolution of 2 to 4 cm^{-1} and KBr pellets. ^{1}H-NMR spectra were taken on a Bruker-WH-90 MHz instrument with D_2O solutions containing *DSS* as reference. Molar conductance measurements were carried out at room temperature in H_2O solution

(10^{-3} *M*) with a conductivity meter type CDM2e (Radiometer Copenhagen). X-ray powder photographs were taken for comparative purpose, using a camera (Philips, *Debye-Scherrer*) with copper K_α radiation.

Results and Discussion

An X-ray structural analysis had shown [10] that the calcium ion in Ca(*L*-arabinose)$Cl_2 \cdot 4H_2O$ is eight-coordinated, binding to two arabinose molecules via O1, O5 of the first, O3, O4 oxygen atoms of the second, and to four H_2O molecules. On the other hand, on the basis of spectral similarities, magnesium [5], zinc [6] and cadmium [6] cations were found to be six-coordinated in the corresponding sugar complexes, binding to two moieties in a similar fashion to that of the Ca(II) ion and the two water molecules. The FT-IR spectra of the metal-arabinose complexes were taken in the region of 4 000–500 cm^{-1} and compared with the corresponding uranyl-arabinose complexes.

L-Arabinose OH *Stretching Vibrations and Coordination Modes*

On the basis of the structural information obtained from X-ray [7] and neutron diffraction measurements [8], there are four distinct hydrogen bonding OH groups in the crystal structure of the *L*-arabinose molecule. According to the hydrogen bonding strengths, based on the intermolecular O...O distances observed in the hydrogen bonding structures of *L*-arabinose, the following relationships are present:

Type of hydrogen bond	H ... O (A°)	O ... O (A°)	νOH (cm^{-1})
O(2)—H ... O(3)H	1.739	2.680	3 235 b
O(3)—H ... O(2)H	1.801	2.747	3 321 sh
O(1)—H ... O(5)	1.820	2.762	3 340 vs
O(4)—H ... O(2)H	2.201	3.020	3 536 s

Thus, the order of the hydrogen bond strengths is as follows: O(2)H > O(3)H > O(1)H > O(4)H.

The four absorption bands observed in the infrared spectrum of the free *L*-arabinose are assigned to the OH stretching vibrations which are summarized below:

A strong absorption band with medium intensity at 3 536 cm^{-1} is related to the unperturbed O(4)H stretching; a strong absorption band at 3 340 cm^{-1} is assigned to the O(1)H stretching; a shoulder at 3 321 cm^{-1} is related to the O(3)H and a broad absorption centered at about 3 235 cm^{-1} is assigned to the strongly hydrogen bonded O(2)H stretching vibration (Table 1).

Table 1. *FT-IR Absorption bands (cm^{-1}) for L-arabinose and its uranyl-adducts in the region of 3 600–500 cm^{-1} with possible band assignments*

L-arabinose	UO_2(*L*-arabinose) $Cl_2 \cdot 2H_2O$	UO_2(*L*-arabinose) $Br_2 \cdot 2H_2O$	UO_2(*L*-arabinose) $(NO_3)_2 \cdot 2H_2O$	Assignments [4–9, 11–13]
3 536 s	3 537 s 3 496 s	3 536 s 3 490 s	3 536 s 3 495 s	} νO_4—H … O_2
3 340 vs	3 350 s 3 333 bs	3 345 s 3 330 mb	3 350 s 3 325 mb	} νO_1—H … O_5
3 321 sh	3 290 s 3 260 m	3 280 s 3 250 s	3 275 b 3 255 s	} νO_3—H … O_2
3 235 b	3 210 b	3 215 b	3 210 b	} νO_2—H … O_3
2 995 w	2 990 w	2 985 w	2 985 w	} $\nu_{as}(CH_2)$ of C_5
2 970 sh	2 975 w	2 980 w	2 985 w	} $\nu(CH)$ of C_4
2 953 m	2 950 m	2 955 m	2 950 m	} $\nu(CH)$ of C_3
2 940 m	2 945 m	2 943 m	2 945 m	} $\nu(CH)$ of C_2
2 891 w	2 885 vw	2 890 w	2 885 w	} $\nu_s(CH_2)$ of C_5
2 864 vw	—	—	—	} $\nu(CH)$ of C_1
—	1 612 vs	1 610 vs	1 628 s	} $\delta(H_2O)$
1 473 m	1 460 sh	1 455 sh	1 468 sh	} $\delta(OCH) + \delta(CCH)$
1 425 w	1 445 sh	1 447 m	—	} $\delta(OCH) + \delta(CCH)$
—	—	—	1 393 bs	} νNO_3^-
1 402 vw	1 414 m	1 410 sh	—	} $\delta(CH_2) + \delta(COH)$

1 371 s	1 390 sh	1 390 w	1 370 s	$\delta(CH_2) + \delta(COH)$
1 357 m	1 353 s	1 359 m	—	$\delta(CCH) + \delta(OCH)$
1 317 s	1 320 vw	1 345 w	1 315 m	$\delta(CCH) + \delta(COH)$
1 257 m	1 230 s	1 259 s	1 269 s	$\delta(CCH) + \delta(COH)$
1 232 m	1 220 sh	1 200 m	1 230 sh	$\delta(COH) + \delta(CCH)$
1 134 vs	1 136 s	1 134 s	1 135 s	$\nu(CO) + \nu(CC)$
1 100 sh	—	1 087 sh	1 088 sh	$\nu(CO) + \nu(CC)$
1 002 s	1 072 bs	1 066 bs	1 058 bs	$\nu(CC) + \nu(CO)$
1 069 s	—	—	—	$\nu(CO)$
1 053 vs	—	—	—	
1 002 s	1 002 s	1 002 s	1 001 vs	$\nu(CO) + \delta(CCO)$
943 m	—	—	—	$\delta(CCH) + \nu(CO)$
—	930 s	933 s	935 vs	$\nu_{antisym.}$ OUO
893 s	855 m	852 s	893 m	$\nu(CC) + \delta(CH)$
842 s	—	842 sh	842 m	$\delta(CH)$
785 s	786 m	777 m	786 s	$\tau(CO) + \delta(CCO)$
713 m	760 w	731 w	775 w	$\delta(CCO) + \delta(OCO)$
677 s	693 s	666 vw	677 s	$\delta(CCO) + \tau(CO)$
627 w	630 sh	629 w	629 sh	$\delta(CO)$
602 m	—	608 sh	605 w	$\tau(CO) + \delta(CCO)$
590 m	568 m	564 w	570 sh	$\tau(CO) + \delta(CCO)$
530 vw	540 m	538 m	539 w	$\delta(CCO) + \delta(OCO)$

s = strong; w = weak; sh = shoulder; m = medium; v = very; b = broad; ν = stretching; δ = bending, and τ = internal rotation

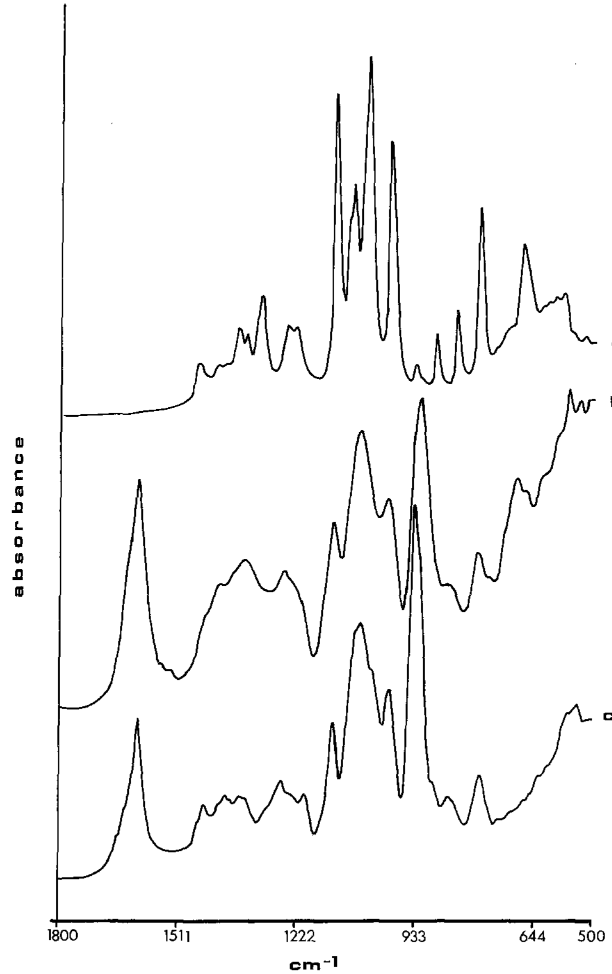

Fig. 1. FT-IR spectra of the free *L*-arabinose and its uranyl adducts in the region of 1 800–500 cm^{-1} for: *a* *L*-arabinose; *b* UO_2(*L*-arabinose)$Cl_2 \cdot 2\,H_2O$; *c* UO_2(*L*-arabinose)$Br_2 \cdot 2\,H_2O$

The OH stretching vibrations of the free *L*-arabinose exhibited considerable changes (shifting and splitting) upon sugar metalation (Table 1). The changes observed for the OH stretching vibrations are due to the participation of the sugar hydroxyl groups in the metal-arabinose bonding. Similar spectral changes were observed in the infrared spectra of the structurally known Ca(*L*-arabinose)$Cl_2 \cdot 4\,H_2O$ and the corresponding magnesium compounds [4, 5], where each metal ion was found to be bonded to two sugar moieties through O(3)H, O(4)H of the first and

O(1)H, O(5) of the second sugar molecule, as well as to 4 or 2 water molecules. Therefore, the uranyl ion is coordinated to two arabinose molecules in a similar fashion with those of the Ca(II) and Mg(II) ions [4, 5].

It should be noted that the rearrangements of the intermolecular sugar hydrogen bonding network to that of the OH...H_2O...Cl^- system observed in the crystal structure of the Ca(*L*-arabinose)$Cl_2 \cdot 4H_2O$ compound [10] are also responsible for the alterations of the sugar OH stretching vibrations. However, it is rather difficult to separate the effect of metalation from that of the alteration of the sugar hydrogen bonding system on the sugar OH stretching frequencies.

L-Arabinose C—H *Stretching Vibrations*

Recently, *Szarek* et al. [11] have assigned the C—H stretching vibrations of the *D*-arabinopyranose. *L*-arabinose has six fundamental C—H stretching vibrations. All of them appeared in the infrared spectrum of the free *L*-arabinose and were assigned to the asymmetric and symmetric stretching vibrations of the CH_2 and CH groups (Table 1) in good agreement with Ref. [11]. The CH stretching vibrations of the free sugar showed no major changes upon complex formation (Table 1).

A strong absorption band at about 1 612–1 630 cm^{-1} appeared in the spectra of these uranyl-arabinose compounds and was attributed to the bending vibration of the hydrated H_2O molecule (Table 1 and Fig. 1). Due to the overlapping of the water OH stretching with those of the sugar OH absorption bands in the region of 3 500–3 200 cm^{-1}, it was difficult to relate any absorption band to the presence of the water OH stretching frequency.

L-Arabinose Ring Vibrational Frequencies and Metal Binding

The ribose ring vibrational frequencies are strongly coupled and the assignment of every individual absorption band to a certain vibrational frequency is difficult to make. However, in recent years isotopic substitution and normal mode coordinate analyses [12, 13] as well as metalation [4, 5, 14] were used to resolve some of the carbohydrate vibrational problems.

The strongly coupled COH and CCH deformation modes [12, 13] of the *L*-arabinose appeared in the region of 1 470–1 230 cm^{-1} and showed major changes (intensity changes and shifting) upon sugar metalation (Fig. 1 and Table 1). The shifts of the COH bending modes towards higher frequencies, together with the shifts of the OH stretching vibrations towards lower frequencies (3 500–3 200 cm^{-1}), are indicative of the participation of the sugar hydroxyl groups, in metal-sugar coordination [1, 4, 5].

The CO stretching vibrations of the ribose ring [12, 13] coupled with the OH bending vibrations observed in the region of 1 100–900 cm^{-1}, in the spectrum of free *L*-arabinose and exhibited drastic changes on complex formation (Fig. 1 and Table 1). The changes observed for the CO stretching vibrations are due to the involvement of the CO oxygen atom in metal-ligand bonding. Similar spectral changes were observed in the infrared spectra of the corresponding Ca(II) and Mg(II)-arabinose complexes [4, 5], where coordination took place through the CO oxygen atom and the hydroxyl groups.

The skeletal deformation modes of the C—O—C—O and the C—C—C groups [12, 13] of the free arabinose appeared in the region of 1 000–500 cm^{-1} and showed changes upon sugar metalation (Fig. 1 and Table 1). Since the ring vibrations are strongly coupled, the metalation of the sugar moiety changes the electron distribution within the ring system (where the vibrations are mostly localized) resulting in a ring distortion, which finally causes the alterations of the ring vibrational frequencies [4, 5].

A strong and broad absorption band at 1 393 cm^{-1} in the spectrum of the UO_2(*L*-arabinose)$(NO_3)_2 \cdot 2H_2O$ compound, which is absent in the spectra of the free sugar and its uranyl halide adducts (Fig. 1 and Table 1) is assigned to the ν_3 of the ionic nitrate in D_{3h} symmetry [15]. This is indicative of the presence of no direct metal-nitrate interaction, which is consistent with the high molar conductivity observed for this compound in aqueous solution. Other absorption bands related to the ionic nitrate [15] at about 1 050 (ν_1), 850 (ν_2) and 740 cm^{-1} (ν_4) are obscured by the vibrations of the arabinose moiety.

A strong absorption band at 930–935 cm^{-1} in the spectra of the uranyl-arabinose adducts (absent in the spectrum of uncoordinated *L*-arabinose) is related to the antisymmetric stretching of the uranyl group [9, 15] (Fig. 1 and Table 1). The symmetric stretching [15] of the O—U—O group at about 900–800 cm^{-1} was overlapped by the vibrational frequencies of arabinose.

Proton-NMR Spectra and Conformation

The proton-NMR spectra of the *D*-arabinose has been studied by *Lemieux* and *Stevens* [16]. The anomeric H_1 chemical shifts of *L*-arabinose observed at 5.22 for the β-anomer and 4.50 ppm for α-anomer (in D_2O) exhibited considerable changes upon metalation. The ratio α/β changed drastically upon uranium coordination. In the free *L*-arabinose solution (D_2O) $\alpha/\beta = 48/52\%$, whereas in the solution of the structurally known Ca(*L*-arabinose)$Cl_2 \cdot 4H_2O$ this ratio changes to $\alpha/\beta = 68/32\%$ (Fig. 2), which is consistent with the structural information reported on this calcium compound [11]. We found an α/β ratio of 64/34% for the

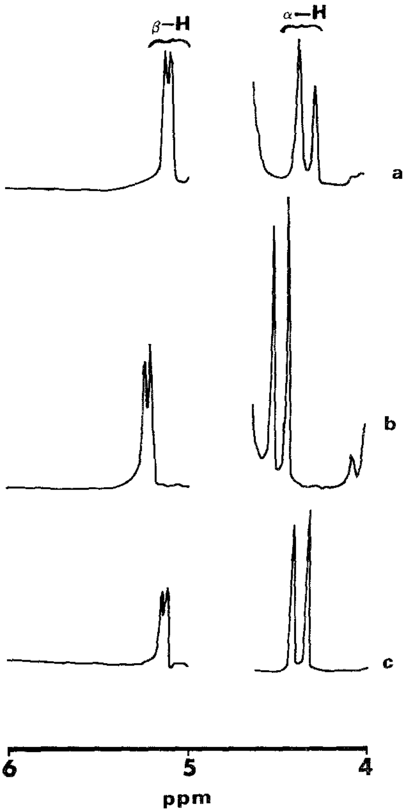

Fig. 2. ^{1}H-NMR of the anomeric proton (H_1) of the free *L*-arabinose and its metal adducts (in D_2O) for: *a* *L*-arabinose; *b* structurally known Ca(*L*-arabinose)$Cl_2 \cdot 4\,H_2O$; *c* UO_2(*L*-arabinose)$(NO_3)_2 \cdot 2\,H_2O$

uranyl-nitrate, 67/33% for uranyl-chloride, and 62/38% for the uranyl-bromide complexes (Fig. 2). A similar behaviour was observed in the proton-NMR spectra of the Zn(II), Cd(II) and Hg(II)- arabinose compounds [6]. The anomeric changes observed are due to the chelation of the *L*-arabinose moiety through the hydroxyl groups, which requires β- to α-anomer configurational transitions.

Molar Conductivity and X-Ray Powder Diffraction

The molar conductivities observed (170–190 $\Omega^{-1}\,cm^2\,mol^{-1}$) in aqueous solutions are indicative of the ionic character of the uranyl-*L*-arabinose complexes and the presence of no direct uranyl-anion interaction. There was also no direct Ca—Cl interaction found in the crystal structure of the Ca(*L*-arabinose)$Cl_2 \cdot 4\,H_2O$ compound [11].

The X-ray powder diagrams of the uranyl-arabinose compounds showed no marked similarities with those of the known 8-coordinated Ca(*L*-arabinose)$Cl_2 \cdot 4\,H_2O$ compound [11], while they exhibited distinct similarities with those of the 6-coordinated Mg-arabinose compounds [5] and the corresponding zinc and cadmium complexes [6]. The observed deviations from the Ca-compound are related in part to the higher coordination number found for the calcium ion (C.N. = 8) with respect to the smaller coordination number of the uranyl ion (C.N. = 6). On the other hand, the similarities observed with the Mg(II), Zn(II), and Cd(II) compounds [5, 6] are due to the similar binding sites and coordination numbers in this series of complexes.

Conclusions

On the basis of X-ray structural information and comparison of the spectroscopic properties of known analoguous complexes with the uranyl-arabinose compounds, the following conclusions may be drawn:

a) The rearrangements of the strong sugar hydrogen bonding network occurred upon metalation;

b) The UO_2^{2+} ion binds to two *L*-arabinose molecules, via the hydroxyl oxygen atoms O3, O4 of the one and O5, O1 of the other molecule, resulting into a 6-coordination geometry around the uranium ion with no direct UO_2-anion interaction and

c) The β-anomer sugar configuration is predominant in the free *L*-arabinose, while the α-anomer conformation is favoured, in the uranyl complexes.

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