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Note

Metal-ion interactions with sugars. Crystal structure and FT-IR study of $PrCl_3$–D-ribose complex

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Abstract—A single-crystal of $PrCl_3\cdot$D-ribose$\cdot 5H_2O$ was obtained from a methanol–water solution and its structure determined by X-ray crystallography. Two configurations of the complex, as a pair of isomers, were found in the single-crystal in a disordered state, which differs from that reported previously. The ligand of one of the complexes is α-D-ribopyranose in the $^4C_1$ conformation, and the ligand of the other is β-D-ribopyranose in the $^1C_4$ conformation. The α:β anomeric ratio is 54:46. Both ligands of the two isomers provide three hydroxyl groups in an axial–equatorial–axial orientation for coordination. The Pr^{3+} ion is nine-coordinated, with five Pr–O bonds from water molecules, three Pr–O bonds from the hydroxyl groups of the D-ribopyranose and one Pr–Cl bond from chloride ion. The hydroxyl groups, water molecules, and chloride ions form an extensive hydrogen-bond network. The IR spectral C–C, O–H, C–O, and C–O–H vibrations are shifted in the complex, compared to those in D-ribose, and the IR results are in accord with those obtained from the X-ray diffraction study.

Keywords: Pr–D-ribose complex; Isomers; Crystal structure; FT-IR

D-Ribose, a component of nucleic acids, is a naturally occurring pentose found in all living cells.[1] Solution studies show that D-ribose exists in aqueous solution as an equilibrium mixture of six tautomers. Among these tautomers, those having an axial–equatorial–axial (ax–eq–ax) sequence of three adjacent hydroxyl groups coordinate readily with metal cations to form 1:1 complexes in hydrophilic solvents. It has been reported that the 'complexing' isomers constitute altogether 43% of the total and are less only to those of talose.[2,3] The multiple 'complexing' configurations in D-ribose solution and the fact that metal cations coexist in biological media suggest that the coordination between them may have biological relevance, and thus studying the metal-ion-binding properties of D-ribose is of particular significance.[4–9]

The interactions of Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, and Tb^{3+} with D-ribose in neutral solutions have been studied by NMR and calorimetric methods,[10–12] and stability constants have been calculated ($<10\ M^{-1}$ in most cases). However, the structures of most of these are undefined, because solid complexes are difficult to obtain. Only five such D-ribose–metal complexes (Ca^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, and Nd^{3+}) to date have been obtained as solids.[13–17]

In this work, a single-crystal of the Pr^{3+} complex of D-ribose was obtained, and its crystal structure was determined by X-ray diffraction. In contrast to the single complex observed in single-crystals of $PrCl_3\cdot$D-ribose$\cdot 5H_2O$[16] and $NdCl_3\cdot$D-ribose$\cdot 5H_2O$[17] reported by Yang et al., two complexes were observed in this study. The complexes reported in this article are similar to those observed in single-crystals of $NdCl_3\cdot$D-ribose$\cdot 5H_2O$, $LaCl_3\cdot$D-ribose$\cdot 5H_2O$ and $CeCl_3\cdot$D-ribose$\cdot 5H_2O$ as reported by our group.[14,15] The vibrational spectra of the title complexes were assigned and interpreted and are in agreement with the crystal structure. The two structures of the title complex are shown in Figure 1. Figure 2 shows the projection of the crystal cell

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in the unit structure of $PrCl_3$·β-D-ribopyranose·$5H_2O$ with its ligand in the $^1C_4$ conformation. The crystal data and structure refinements of the complex are listed in Table 1.

As shown in Figure 1, there are two different $PrCl_3$·D-ribose·$5H_2O$ complexes in the single crystal. The ribose moiety of one of them is in the α-pyranose form in the $^4C_1$ conformation (shown by solid bonds in Fig. 1); such a structure has been reported by Yang et al.[16] In the other complex, the ribose moiety is the β-pyranose form in the $^1C_4$ conformation (shown by open bonds in Fig. 1; atoms labeled by primed numbers), which has not been observed previously. The α/β anomeric ratio is 54:46. In both of the $PrCl_3$·D-ribose·$5H_2O$ complexes, the Pr ion is nine-coordinated and binds to three hydroxyl groups of one D-ribopyranose molecule, five water molecules, and a chloride ion. The other two chloride ions in the molecule are not bound to the complex. The three adjacent hydroxyl groups labeled O(1)H, O(2)H, and O(3)H (α-ribopyranose $^4C_1$ conformation) or O(2′)H, O(3′)H, and O(4′)H (β-ribopyranose $^1C_4$ conformation), containing the ax–eq–ax sequence, are the coordination sites of the ribose. The Pr–O distances at the coordination sites (2.483–2.710 Å in the β-pyranose isomer, and 2.500–2.586 Å in the α-pyranose isomer) are comparable to those reported by Yang et al. (2.535–2.589 Å).[16] The ring oxygen of D-ribose does not coordinate with Pr^{3+} in either molecule. All water molecules in the crystal are coordinated in the two complexes. The coordination

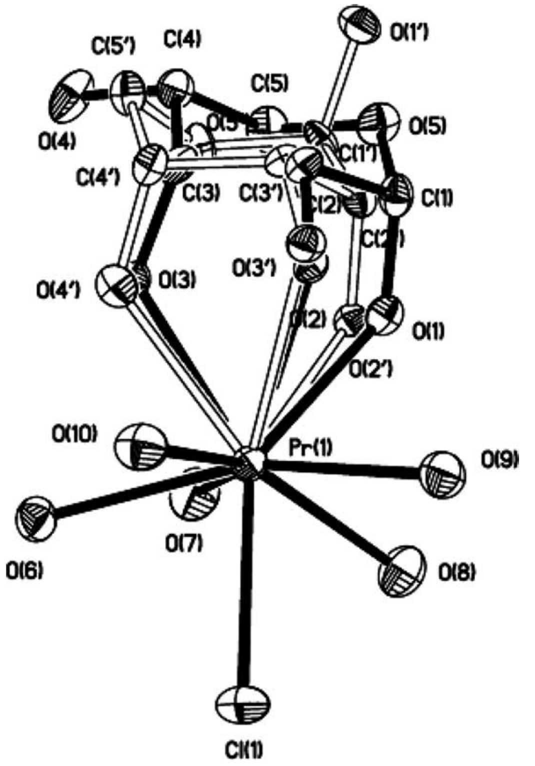

Figure 1. The structure and atom numbering scheme of the $[Pr(\alpha/\beta\text{-D-ribopyranose})(H_2O)_5Cl]^{2+}$ ion (hydrogen atoms have been omitted for clarity). There are two $PrCl_3$·D-ribose·$5H_2O$ complexes in the single crystal. One, shown by solid bonds is α-D-ribopyranose, is in the $^4C_1$ conformation, and the other, shown by open bonds, is β-D-ribopyranose in the $^1C_4$ conformation (primed numbers).

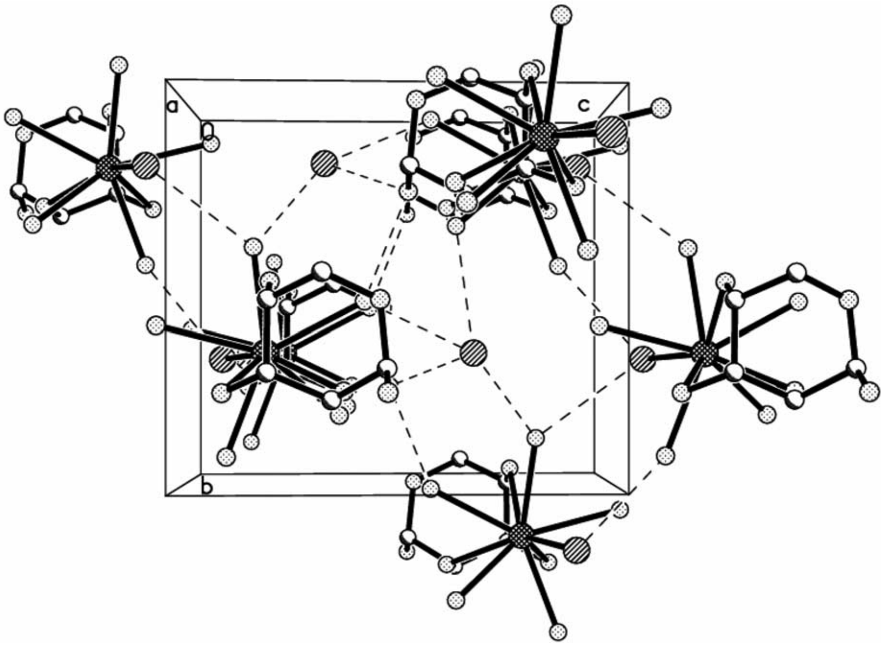

Figure 2. Projection of the crystal cell in the structure of $PrCl_3$·D-ribose·$5H_2O$. The ligand shown is β-D-ribopyranose in the $^1C_4$ configuration. The spheres are defined as follows: ▨ = Cl, ● = Pr, ◌ = O, ○ = C.

Table 1. Crystal data and structure refinement parameters for $PrCl_3$·D-ribose·$5H_2O$

Formula	$PrCl_3$·D-ribose·$5H_2O$
Formula weight	487.47
Crystal system, space group	Monoclinic, *P*2(1)
a (Å)	9.2007(14)
b (Å)	8.8274(14)
c (Å)	9.8291(16)
β (°)	93.971(5)
V ($Å^3$)	796.4(2)
Z	2
D_{calcd} (Mg/m^3)	2.033
Absorption coefficient (mm^{-1})	3.599
F (000)	480
Crystal size (mm)	0.16 × 0.14 × 0.10
θ Range for data collection (°)	2.08–26.38
Index ranges	$-11 \leqslant h \leqslant 11$, $-10 \leqslant k \leqslant 10$, $-12 \leqslant l \leqslant 9$
Reflections collected/unique	2974/2536 [*R*(int) = 0.0309]
Completeness to θ	97.7% ($\theta = 26.38$)
Absorption correction	Semi-empirical from equivalents
Max/min transmission	0.7148 and 0.5967
Refinement method	Full-matrix least-squares on F^2
S	0.965
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0387$, $wR2 = 0.0716$
R indices (all data)	$R1 = 0.0606$, $wR2 = 0.0787$
Absolute structure parameter	0.01(3)
Largest difference peak and hole (e/$Å^3$)	0.672 and −0.708
Data/restraints/parameters	2536/0/265
α/β Anomer ratio	54:46

behavior of La^{3+}, Ce^{3+}, Pr^{3+}, and Nd^{3+} are shown to be similar.

An extensive network of hydrogen bonds involving all hydroxyl groups, water molecules, and chloride ions in the crystal of $PrCl_3$·D-ribose·$5H_2O$, which has not been reported previously, was present (data given in the Supplementary data). The Pr–ribose complexes are organized by these hydrogen bonds and thus form layers parallel to the (1 0 −1) plane. These layers are also held together by hydrogen bonds with regular spaces between them. The free chloride ions distributed in these layers are responsible not only for the formation of the layer but also the bonding between the layers by hydrogen bonds. This network of hydrogen bonds forms the packed structure of the whole crystal. In the $PrCl_3$·D-ribose·$5H_2O$ complex, the chloride ions play important roles not only as counterions but also as a predominant feature in the network of hydrogen bonds.

Our group has measured IR data of a series of metal–ribose complexes. For purposes of comparison, the FT-IR spectra of D-ribose and its complexes (La–D-ribose, Ce–D-ribose, Pr–D-ribose, and Nd–D-ribose complexes) are shown in Figure 3, and the absorption bands and tentative assignments are collected in Table 2. These results show that the IR data of La–, Ce–, Pr–, and Nd–D-ribose complexes, including those reported by Yang et al. are similar, indicating that La^{3+}, Ce^{3+}, Pr^{3+}, and Nd^{3+} have similar coordination modes.

The broad absorption band at around 3400 cm^{-1} in the spectrum of D-ribose can be assigned to the hydrogen-bonded OH groups. This band is broader in the spectra of its metal complexes (see Fig. 3). The observed changes are due to the metalation of the sugar and the rearrangement of the strong hydrogen-bonding network observed in the crystal structures of the complexes (Table 2). The C–H stretching vibration bands in the spectrum of the title complex (2947, 2848, 2673, 2539 cm^{-1}), corresponding to the band of 2928 cm^{-1} in the spectrum of free D-ribose, are weaker and masked by the broadened νOH bands. The band around 1622 cm^{-1} in the spectrum of the complex can be assigned to the δ_{HOH} vibration of the coordinated water. The bands at 1452, 1417, 1340, 1250 cm^{-1} in the spectrum of free D-ribose (Table 2), which was assigned to the multiple bending vibrations of O–C–H, C–C–H, C–O–H, and CH_2, are observed to be shifted in the spectrum of the complex and the intensity is weaker (Fig. 3). The band at approximately 1150 cm^{-1} is a characteristic vibration of a pyranose ring,[19] and it is observed in the spectrum of the title complex and D-ribose itself. In the 1200–970 cm^{-1} region, the C–O, C–C stretching vibrations and the C–O–H, C–C–O bending vibrations of D-ribose are observed to be shifted and split in the spectrum of the complex (Fig. 3 and Table 2). The observed splitting and shifting of absorbances is indicative of the participation of the sugar hydroxyl groups in metal–ligand binding, which therefore affects the C–O, C–C

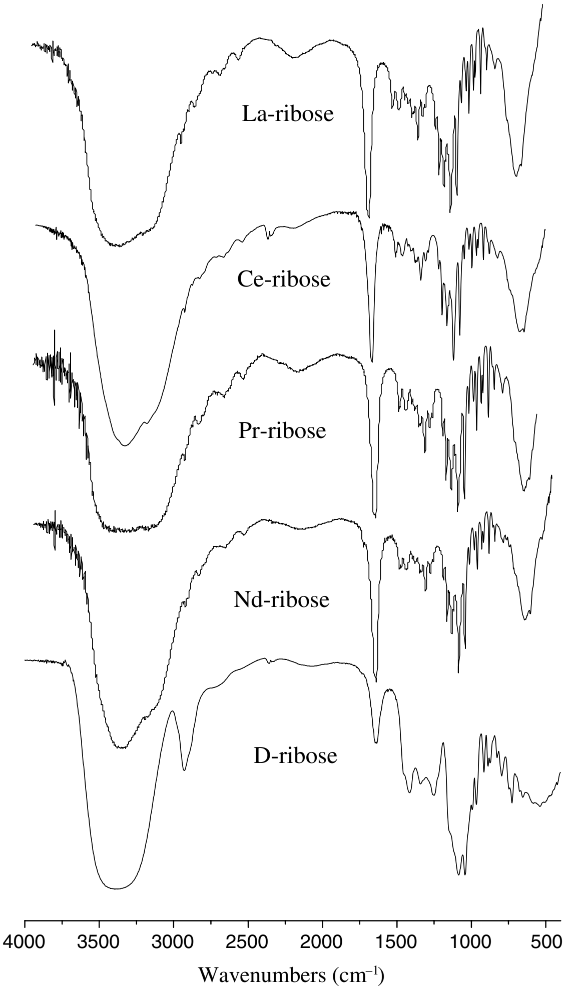

Figure 3. Mid-IR spectra of D-ribose, and La–, Ce–, Pr–, and Nd–D-ribose complexes.

stretching vibrations and the C–O–H, C–C–O bending vibrations of the sugar moiety.

The ring skeletal deformation bands (δC–C–O and δC–C–C) of free D-ribose, mainly in the 1000–400 cm^{-1} region, show considerable changes on complex formation (Fig. 3 and Table 2). This may be attributed to distortion of the sugar ring upon metalation. However, no crystal structure for free D-ribose has been reported, which does not allow comparison with those of the complex. The spectral changes observed in this region may be interpreted to indicate that metalation of the sugar perturbs the electron distribution within the sugar ring system, where the vibrations are mostly localized, and finally causes ring distortion, resulting in the alterations in the spectra. The 914 and 795 cm^{-1} bands in the D-ribose spectrum are attributed to the asymmetric and symmetric ring-breathing modes of the pyranose. They are observed as bands at around 917 and 795 cm^{-1} in the Pr–ribose complex (Table 2), indicating that the six-membered sugar ring is retained in the complex. The absorption bands at about 870 and 840 cm^{-1} in a pyranose spectrum are generally assigned to the presence of the β- and α-anomers, respectively.[20,21] In relation to the spectrum of the title complex, the coexistence of the absorption bands at about 874 and 836 cm^{-1} indicates that the complex is, in fact, a mixture with both α-ribopyranose and β-ribopyranose as ligands, and the two configurations of the complex indicated by the IR data are in accord with the X-ray results. The two absorption bands were also observed in the spectrum of the Pr–ribose complex reported by Yang et al.,[16] indicating that the product they obtained should also be a mixture of both α- and β-anomers, but not only as a single configuration in the α-form as reported.

Table 2. IR data for D-ribose, La–D-ribose, Ce–D-ribose, Pr–D-ribose, and Nd–D-ribose complexes (1500–700 cm^{-1})

D-Ribose	La–ribose	Ce–ribose	Pr–ribose[16]	Pr–ribose[a]	Nd–ribose[14]	Possible assignment[19–24]
1452	1457	1458	1458	1458	1456	δOCH + δCCH + $\delta \mathrm{CH}_2$
1417	1410	1417	1409	1411	1408	δOCH + δCCH
1340	1348	1348	1350	1349	1350	δOCH + δCCH + δCOH
	1319	1318	1318	1317	1315	δOCH + δCCH + δCOH
1250	1244	1244	1244	1244	1244	δCCH + δCOH + δOCH
1153	1152	1153	1152	1151	1153	νC–O + νC–C + δCOH (pyranose)
1117	1128	1127	1128	1128	1128	νC–O + νC–C + δCOH
1085	1093	1094	1095	1094	1091	νC–O + νC–C + δCOH
1042	1047	1047	1048	1048	1047	νC–O + νC–C + δCCO
	1004	1004	1004	1004	1003	νC–O + νC–C + δCCO
987	971	971	972	972	971	νC–O + νC–C + δCCO
914	917	917	918	917	918	νC–O + δCCH + ν asy(ring of pyranose)
887	885	886	887	886	888	νC–O + νC–C + δCCH
872	874	874	874	874	874	δCH(β-pyranose)
	835	835	836	836	836	δCH(α-pyranose)
826						δCH
795	793	794	795	795	796	τC–O + δCCO + δCCH + ν sy(ring of pyranose)
746	734	735	736	736	734	τC–O + δCCO + δCCH

δ, bending mode; ν, stretching mode; τ, twisting.

[a] IR data obtained in this work.

The IR results indicate that the hydroxyl groups of D-ribose take part in metal–oxygen interactions. The hydrogen-bond network rearranges upon metalation and there are two isomers coexisting in the complex with both α-ribopyranose and β-ribopyranose as ligands. The IR results are in accord with those of X-ray diffraction and the FT-IR technique is thus a useful method for detecting the formation of such complexes.

1. Experimental

1.1. Materials

$PrCl_3$ was prepared from the corresponding rare earth oxide of high purity (99.99%).[18] D-Ribose was purchased from Acros, and was used without further purification.

1.2. Preparation of $PrCl_3$·D-ribose·$5H_2O$

D-Ribose (0.45 g, 3 mmol) and equivalent amounts of $PrCl_3$ were dissolved in H_2O–CH_3OH and the solution was evaporated slowly until crystallization occurred. Anal. Calcd for $PrCl_3 \cdot C_5H_{10}O_5 \cdot 5H_2O$: C, 12.32; H, 4.14. Found: C, 12.24; H, 4.20.

1.3. Physical measurements

The mid-IR spectrum was measured on a Nicolet Magna-IR 750 spectrometer using the micro-IR method, 128 scans at 4 cm^{-1} resolution.

The structure of $PrCl_3$·D-ribose·$5H_2O$ was determined on a Bruker SMART 1000 CCD detector/PLATFORM diffractometer using monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) in the θ range from 2.08° to 26.38° at 293 K. The final cycle of full-matrix least-squares refinement was based on 2536 observed reflections. Calculations were completed with the SHELX-97 program.

Crystallographic data (without structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-220666. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [http://www.ccdc.cam.ac.uk; Fax: +44 1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2005.12.011.

References

1. Pauly, D. F.; Pepine, C. J. *J. Cardiovasc. Pharmacol. Ther.* **2000**, *5*, 249–258.
2. Desrosiers, N. M.; Morel, J. P. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 3461–3469.
3. Angyal, S. J. *Pure Appl. Chem.* **1973**, *35*, 131–146.
4. Templeton, D. M.; Sarkar, B. *Biochem. J.* **1985**, *230*, 35–42.
5. Sauchelli, V. *Trace Elements in Agriculture*; Van Nostrand: New York, 1969; p 248.
6. Holm, R. P.; Berg, J. M. *Pure Appl. Chem.* **1984**, *56*, 1645–1657.
7. Predki, P. F.; Whitfield, D. M.; Sarkar, B. *Biochem. J.* **1992**, *281*, 835–841.
8. Weis, W. I.; Drickamer, K.; Hendrickson, W. A. *Nature* **1992**, *360*, 127–134.
9. Drickamer, K. *Nature* **1992**, *360*, 183–186.
10. Alvarez, A. M.; Desrosiers, N. M.; Morel, J. P. *Can. J. Chem.* **1987**, *65*, 2656–2660.
11. Desrosiers, N. M.; Lhermet, C.; Morel, J. P. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2173–2177.
12. Desrosiers, N. M.; Lhermet, C.; Morel, J. P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1223–1228.
13. Lu, Y.; Deng, G. C.; Miao, F. M.; Li, Z. M. *J. Inorg. Biochem.* **2003**, *96*, 487–492.
14. Lu, Y.; Deng, G. C.; Miao, F. M.; Li, Z. M. *Carbohydr. Res.* **2003**, *338*, 2913–2919.
15. Lu, Y.; Deng, G. C.; Miao, F. M.; Li, Z. M. *Carbohydr. Res.* **2004**, *339*, 1689–1696.
16. Yang, L. M.; Zhao, Y.; Xu, Y. Z.; Jin, X. L. *Carbohydr. Res.* **2001**, *334*, 91–95.
17. Yang, L. M.; Wu, J. G.; Weng, S. F.; Jin, X. L. *J. Mol. Struct.* **2002**, *612*, 49–57.
18. Chandrasekhar, A. *J. Imaging Technol.* **1990**, *16*, 158–161.
19. Cael, J. J.; Koenig, J. L.; Blackwell, J. *Carbohydr. Res.* **1974**, *32*, 79–91.
20. Tajmir-Riahi, A. H. *Carbohydr. Res.* **1983**, *122*, 241–248.
21. Tajmir-Riahi, A. H. *Carbohydr. Res.* **1984**, *127*, 1–8.
22. Zhang, W. J. *Biochemical Technology of Complexes of Carbohydrates*; Zhejiang University Press: Hangzhou, 1999; pp 193–198.
23. Mathlouthi, M.; Seuvre, A. M.; Koenig, J. L. *Carbohydr. Res.* **1983**, *122*, 31–47.
24. Tajmir-Riahi, A. H. *Biophys. Chem.* **1986**, *23*, 223–228.