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Metal Ion Interactions with Sugars: Crystal Structure and FT-IR Study of the EuCl_3 -Ribose Complex

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A single-crystal of $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$ was obtained from methanol-water solution and its structure determined by x-ray analysis. Two configurations of the complex, as a pair of anomers, were found in the single crystal in a disordered state, which is different from that reported previously.^[16,17] The ligand of one of the isomers is α -D-ribofuranose in the ⁴C₁ conformation, and the ligand of the other is β -D-ribofuranose in the ¹C₄ conformation. The α : β anomeric ratio is 52:48. Both ligands of the two isomers provide three hydroxyl groups in ax-eq-ax orientation for coordination. The Eu^{3+} ion is nine-coordinated with five Eu-O bonds from water molecules, three Eu-O bonds from hydroxyl groups of the D-ribofuranose, and one Eu-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 were observed to be shifted in the complex and the IR results are in accord with those of x-ray diffraction.

Keywords D-ribose; Eu-D-ribose complex; Isomers, Crystal structure; FT-IR

INTRODUCTION

D-Ribose ($\text{C}_5\text{H}_{10}\text{O}_5$), 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 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 43% of

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the total, less than those only of talose.^[2,3] The multiple “complexing” configurations in solutions of D-ribose and the fact that metal cations coexist in biological fluids suggest that the coordination between them may have some biological relevance, and studying the metal ion-binding properties of D-ribose may have 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 the stability constants have been calculated ($<10 \text{ M}^{-1}$ in most cases). However, the structures of most of these generated complexes are still undefined, because solid complexes are difficult to obtain. Only six ribose-metal complexes, from Ca^{2+} , La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , and Sm^{3+} , have so far been obtained as solids.^[13–18]

In this work, a single-crystal of Eu^{3+} complex from D-ribose was obtained, and its crystal structure was determined by x-ray analysis. In contrast to the single configuration observed in the single crystals of $\text{PrCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$ ^[16] and $\text{NdCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$ ^[17] reported by Yang et al., two configurations were observed in the single crystal of the D-ribose–Eu complex. The vibrational spectra of the title complex were assigned and interpreted in correlation with the crystal structure.

RESULTS AND DISCUSSION

X-Ray Crystal Structures

The single crystal of the title complex exists in a disordered state with two configurations, as a pair of anomers, and the structures are similar to those of $\text{NdCl}_3 \cdot \text{ribose} \cdot 5\text{H}_2\text{O}$ reported by our group.^[14] The two structures of the title complex are shown together in Figure 1. Figure 2 is the projection of the crystal in the unit cell structure of $\text{EuCl}_3 \cdot \alpha\text{-ribopyranose} \cdot 5\text{H}_2\text{O}$ with its ligand in ${}^4\text{C}_1$ conformation. The crystal data and structure refinements of the complex are listed in Table 1.

Figure 1 shows that there are two kinds of $\text{EuCl}_3 \cdot \text{ribose} \cdot 5\text{H}_2\text{O}$ molecules with different configurations in the single crystal. The ribose moiety of one of the molecules is the α -pyranose in the ${}^4\text{C}_1$ conformation (shown by solid bands in Fig. 1). In the other $\text{EuCl}_3 \cdot \text{ribose} \cdot 5\text{H}_2\text{O}$ molecule, the ribose moiety is the β -pyranose in the ${}^1\text{C}_4$ conformation (shown by open bands in Fig. 1 and the atoms labeled by numbers with dashes). The $\alpha:\beta$ anomeric ratio is 52:48. In both of the $\text{EuCl}_3 \cdot \text{ribose} \cdot 5\text{H}_2\text{O}$ molecules, the Eu 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 Cl ions in the molecule are free. The three adjacent hydroxyl groups labeled O(1)H, O(2)H and O(3)H (in the α -ribopyranose ${}^4\text{C}_1$ conformation) or O(2')H, O(3')H and O(4')H (in the

Table 1: Crystal data and structure refinement parameters for $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$

Formula	$\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$
Formula weight	498.52
Crystal system, space group	Monoclinic, $P2(1)$
a (Å)	9.242(10)
b (Å)	8.962(9)
c (Å)	9.987(11)
β (°)	94.324(16)
V (Å ³)	824.8(15)
Z	2
D calcd (mg/m ³)	2.007
Absorption coefficient (mm ⁻¹)	4.323
$F(000)$	488
Crystal size (mm)	0.15 × 0.12 × 0.10
θ Range for data collection (°)	2.05–26.52
Index ranges	$-11 \leq h \leq 8, -8 \leq k \leq 11, -12 \leq l \leq 12$
Reflections collected/unique	3728/2567 (R(int) = 0.0489)
Completeness to $\theta = 26.52(\%)$	97.7
Absorption correction	Semi-empirical from equivalents
Max/min transmission	0.6717 and 0.5633
Refinement method	Full-matrix least-squares on F^2
S	0.995
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0459, wR2 = 0.0771$
R indices (all data)	$R1 = 0.0764, wR2 = 0.0877$
Absolute structure parameter	-0.01(3)
Largest difference peak and hole (e/Å ³)	1.374 and -1.455
Data/restraints/parameters	2567/573/265

β -ribopyranose 1C_4 conformation), which contain the ax-eq-ax sequence, are the coordination sites of the ribose, and the Eu-O distances at the coordination sites (from 2.43 to 2.63 Å in the β -pyranose 1C_4 conformation, and from 2.54 to 2.58 Å in the α -pyranose 4C_1 conformation) are comparable to those reported by Yang et al. (from 2.535 to 2.589 Å). The ring oxygen of D-ribose does not coordinate with Eu^{3+} in either molecule. All water molecules in the crystal are coordinated in the two structures.

An extensive network of hydrogen bonds involving all hydroxyl groups, water molecules, and chloride ions in the crystal of $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$ was determined in this work, and the data are given in Table 2. The Eu-ribose complex molecules are organized by these hydrogen bonds and thus form layers parallel to the (1 0 -1) plane. These layers are then also held together by hydrogen bonds with regular spaces between them. Free Cl ions distributed in these layers are responsible for not only the formation of a 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 $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$

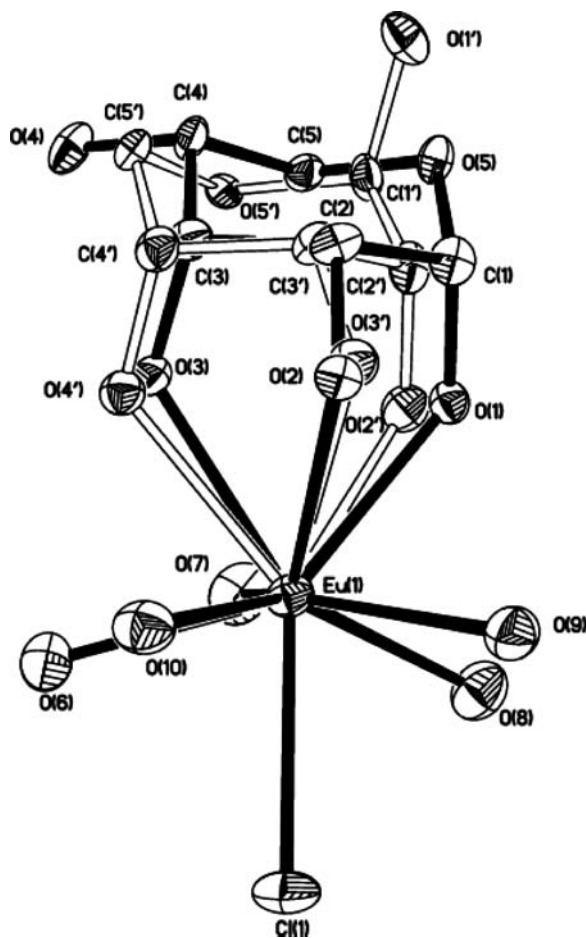


Figure 1: The structure and atom numbering scheme of the $(\text{Eu}(\alpha/\beta\text{-D-ribose})(\text{H}_2\text{O})_5\text{Cl})^{2+}$ ion (hydrogen atoms have been omitted for clarity). The ligand of the complex is in a disordered state, which indicates that there are two configurations of $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$ molecules in the single crystal. The one shown by solid bands is α -D-ribose in the ${}^4\text{C}_1$ conformation, and the other shown by open bands is β -D-ribose in the ${}^1\text{C}_4$ conformation (labeled by numbers with dashes).

complex, the Cl ions play important roles not only as counterions but also as the predominant feature in the network of hydrogen bonds.

IR Spectroscopy Study of Eu-ribose Complex

The FT-IR spectra of D-ribose and the Eu^{3+} salt are shown in Figure 3. The IR data of a series of metal-ribose complexes have also been measured, and for comparing, the data are shown together in Table 3. The tentative assignments are also given. Table 3 shows that the IR data of the Ln-ribose complexes

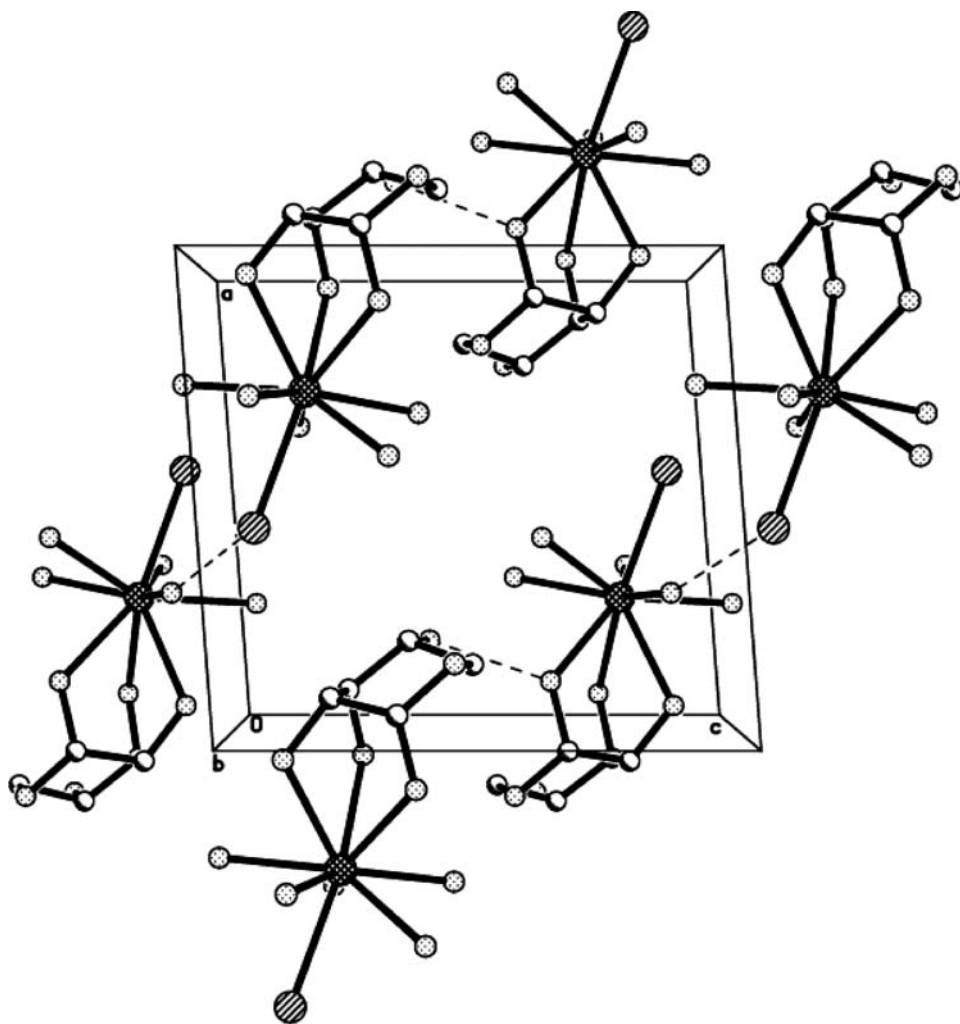


Figure 2: Projection of the crystal cell in the structure of $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$. The ligand shown is α -D-ribose in the ${}^4\text{C}_1$ configuration.

are similar, indicating that the lanthanide series have similar coordination mode.

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 appears broader in the spectra of its metal complexes. The observed spectral 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 (see Table 2). The band at about 1150 cm^{-1} is the characteristic vibration of a pyranose,^[21] and it is observed in the spectrum of the title complex and

Table 2: Hydrogen bonds for $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$ with $\text{H} \dots \text{A} < r(\text{A}) + 2.000 \text{ \AA}$ and $\langle \text{DHA} \rangle > 110^\circ$

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\langle \text{DHA} \rangle$
O6-H6A...Cl3#1	0.850	2.572	3.244	136.72
O6-H6B...Cl2#2	0.856	2.707	3.524	160.12
O7-H7B...O5 #3	0.850	2.125	2.948	162.79
O7-H7B...O1' #3	0.850	2.148	2.760	128.68
O8-H8A...Cl3	0.850	2.456	3.302	173.14
O8-H8B...O4 #4	0.850	2.383	3.108	143.56
O8-H8B...Cl3#2	0.850	2.868	3.559	139.63
O9-H9A...Cl1#5	0.850	2.453	3.206	147.95
O9-H9B...Cl2#6	0.850	2.393	3.238	172.62
O10-H10A...Cl3#7	0.856	2.692	3.301	129.24
O10-H10B...Cl2#8	0.856	2.361	3.173	158.33
O1-H1...O4 #4	0.930	1.772	2.681	164.82
O2-H2...Cl2#8	0.930	2.400	3.004	122.52
O3-H3...Cl2#2	0.930	2.550	3.228	130.03
O4-H4...Cl3#9	0.820	2.444	3.253	169.42
O1'-H1'...O7 #4	0.820	2.333	2.760	113.11
O2'-H2'...O5' #4	0.930	2.416	2.969	118.05
O3'-H3'...Cl2#8	0.930	2.768	3.191	108.7
O4'-H4'...Cl2#2	0.930	2.142	2.970	147.78

Symmetry transformations used to generate equivalent atoms: #1 $x, y-1, z$; #2 $-x+1, y-1/2, -z+1$; #3 $-x, y-1/2, -z+1$; #4 $-x, y+1/2, -z+1$; #5 $-x+1, y+1/2, -z+2$; #6 $-x+1, y+1/2, -z+1$; #7 $-x+1, y-1/2, -z+2$; #8 $x-1, y, z+1$; #9 $x-1, y-1, z$.

D-ribose itself. In the $1200\text{--}970 \text{ cm}^{-1}$ 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 (see Table 3). Such observed splitting and shifting is indicative of the participation of the sugar hydroxyl

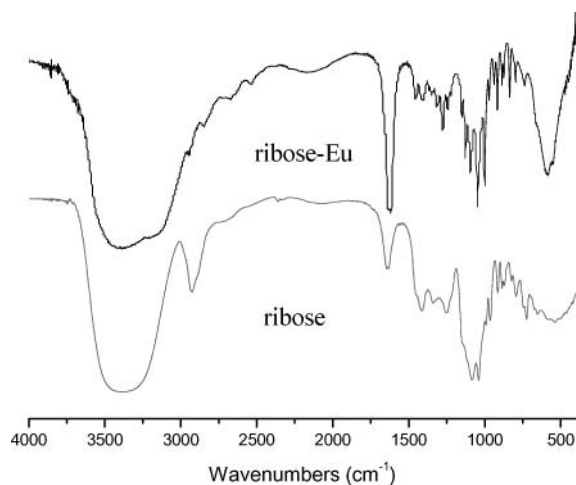
**Figure 3:** The mid-IR spectra of D-ribose and Eu-ribose.

Table 3: IR data for D-ribose, Pr-ribose, Nd-ribose, and Eu-ribose complexes (1500–700 cm⁻¹)

D-ribose	Pr-ribose ⁽¹⁶⁾	Nd-ribose ⁽¹⁴⁾	Eu-ribose	Possible assignment ^(20–25)
1452	1458	1456	1456	$\delta\text{OCH} + \delta\text{CCH} + \delta\text{CH}_2$
1417	1409	1408	1408	$\delta\text{OCH} + \delta\text{CCH}$
1340	1350	1350	1350	$\delta\text{OCH} + \delta\text{CCH} + \delta\text{COH}$
	1318	1315	1317	$\delta\text{OCH} + \delta\text{CCH} + \delta\text{COH}$
1250	1244	1244	1244	$\delta\text{CCH} + \delta\text{COH} + \delta\text{OCH}$
1153	1152	1153	1152	$\nu\text{C-O} + \nu\text{C-C} + \delta\text{COH}$ (pyranose)
1117	1128	1128	1128	$\nu\text{C-O} + \nu\text{C-C} + \delta\text{COH}$
1085	1095	1091	1095	$\nu\text{C-O} + \nu\text{C-C} + \delta\text{COH}$
1042	1048	1047	1049	$\nu\text{C-O} + \nu\text{C-C} + \delta\text{CCO}$
	1004	1003	1003	$\nu\text{C-O} + \nu\text{C-C} + \delta\text{CCO}$
987	972	971	972	$\nu\text{C-O} + \nu\text{C-C} + \delta\text{CCO}$
914	918	918	917	$\nu\text{C-O} + \delta\text{CCH} + \nu\text{sy}(\text{ring of pyranose})$
887	887	888	887	$\nu\text{C-O} + \nu\text{C-C} + \delta\text{CCH}$
872	874	874	875	$\delta\text{CH} (\beta\text{-pyranose})$
	836	836	836	$\delta\text{CH} (\alpha\text{-pyranose})$
826				δCH
795	795	796	799	$\tau\text{C-O} + \delta\text{CCO} + \delta\text{CCH} + \nu\text{sy}(\text{ring of pyranose})$
746	736	734	738	$\tau\text{C-O} + \delta\text{CCO} + \delta\text{CCH}$

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

groups in metal ligand bonding, which therefore affects the C-O, C-C stretching vibrations and the C-O-H, C-C-O bending vibrations of the sugar moiety.

The ring skeletal deformation bands ($\delta\text{C-C-O}$ and $\delta\text{C-C-C}$) of free D-ribose, mainly in the 1000–400 cm⁻¹ region, show considerable changes on complex formation (see Table 3). These may be attributed to distortion of the sugar ring upon metalation. However, no crystal data for free D-ribose have been reported to permit comparison with those of the complex. The 914 cm⁻¹ and the 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 799 cm⁻¹ in the Eu-ribose complex (see Table 3), 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.^[21,22] In relation to the spectrum of the title complex, the coexistence of the absorption bands at about 875 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.

CONCLUSION

Two configurations of the D-ribose–Eu complex, as a pair of anomers, were found in the single crystal in a disordered state, which is different from that reported previously.^[16,17] The ligand of one of the isomers is α -D-ribofuranose in the 4C_1 conformation, and the ligand of the other is β -D-ribofuranose in the 1C_4 conformation. The α : β anomeric ratio is 52:48. Both ligands of the two isomers provide three hydroxyl groups in ax-eq-ax orientation for coordination. The IR results indicate that the hydroxyl groups of D-ribose take part in the metal-oxygen interaction; the hydrogen-bond network rearranges upon metalation; and there are two isomers coexisting in the complex with both α -ribofuranose and β -ribofuranose 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.

EXPERIMENTAL

Materials

EuCl_3 was prepared from corresponding rare earth oxide of high purity (99.99%).^[20] D-Ribose was purchased from Acros, and was used without further purification.

Preparation of $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$

D-Ribose (4 mmol) and equivalent amounts of EuCl_3 were dissolved in H_2O -MeOH, and the solution was evaporated slowly until crystallization occurred.

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 $\text{EuCl}_3 \cdot \text{C}_5\text{H}_{10}\text{O}_5 \cdot 5\text{H}_2\text{O}$ was determined on a Bruker SMART 1000 CCD detector/PLATFORM diffractometer using monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in the θ range from 2.05 to 26.52° at 293 K. The final cycle of full-matrix least-squares refinement was based on 2567 observed reflections. Calculations were completed with the SHELX-97 program.

SUPPLEMENTARY MATERIAL

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-199657. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [<http://www.ccdc.cam.ac.uk>; Fax: (international) +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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