Oxidorhenium(V) complexes with L-histidine and pyranosides†

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The reaction of the oxidorhenium(V) precursor [$ReOCl_3(PPh_3)_2$] with the proteinogenic amino acid L-histidine (L-hisH) and the glycosides methyl α-D-mannopyranoside (Me-α-D-Man*p*) and methyl β-D-ribopyranoside (Me-β-D-Rib*p*) in methanol/triethylamine yielded the crystalline compounds [ReO(L-his)(Me-α-D-Man*p*2,3H_{-2})]·2MeOH (1) and [ReO(L-his)(Me-β-D-Rib*p*3,4H_{-2})]·$\frac{1}{2}$MeOH (2). The mixed-ligand complexes based on the $Re^{V}O$ moiety were characterised by single-crystal X-ray diffraction, NMR spectroscopy, elemental analysis and mass spectrometry. Both complexes are hydrolytically stable over prolonged periods of time and are accessible also by a purely aqueous route by replacing the rhenium(V) precursor with a perrhenate/reductant couple.

The aqueous coordination chemistry of rhenium and its lighter homologue, technetium, has been largely motivated by their radiotherapeutic use. Suitable oxidation-state–ligand combinations have to meet specific requirements which arise from their attempted application to recognise and/or attack tumour cells. Hence, matter-of-course parameters such as sufficient hydrolytic stability coincide with more sophisticated ones such as the need for a route to couple the rhenium core to biomolecules such as tumour-directed antibodies. In agreement with the many-sided requirements, various strategies have been developed to meet them. A common feature of the currently used concepts is to separate a rhenium-chelating function from another, remote, function which provides a biomolecule coupling site.[1,2] The, by far, most significant acceptor of the rhenium-chelating site is a tricarbonylrhenium(I) fragment.[3-5] (It should be noted that most of the published work has been devoted to the tricarbonyltechnetium(I) core and was applied to the heavier homologue in a supplementing way.) Despite the importance of the tricarbonylmetal(I) fragments, there is a permanent interest to develop chelators for other binding modes of the central metal. In a survey of the currently investigated ligands, various kinds of donor sets are tailored to meet the requirements of the various oxidation states of the central metals.[6] For rhenium, the oxidorhenium(V) core, in particular, provides an alternative to the well-established $Re^{I}(CO)_3$ fragment. Since five ligand-bonding positions are usable with the $Re^{V}O$ core, more degrees of freedom are available to tailor the ligand sphere—a property that is shared by the related $Tc^{V}N$ core.[7] Most commonly, the '3+2' strategy is used to bind a tridentate and a bidentate ligand to the $Re^{V}O$ fragment.[8] Examples include N_2O+O_2 donor sets as used in this work.[9] It might be expected, in view of the attempted application, that biomolecules are particularly promising candidates to provide the required multidentate ligands. In fact, amino acids, nucleobases, as well as carbohydrates have been considered parts of rhenium-chelating entities. However, it is mostly not their pattern of unmodified functional groups that is intended as the rhenium chelator in current work. Instead, the usual procedure is to extend a suitable functional group of the biomolecule to a strongly chelating site by the addition of established ligands such as aromatic amines or ethylene diamine fragments. Examples include the transformation of a weakly coordinating lysine side chain to a tridentate N_3-type chelator as well as the synthesis of a polydentate *N*-glycoside from a reducing sugar.[2,10] Hence, only few unmodified biomolecules have been bonded to the $Re^{V}O$ core.[11-18] Even fewer oxidorhenium(V) complexes, which bear unmodified biomolecules as the only ligands, have been published.[11,12,15,17,18] Reasons for the limited use of solely bioligands seem to have their origin in often unsuitable properties of the complexes. Thus, the Beauchamp group reported that the bis-histidine complex $[ReO(L\text{-}his)_2]^+$ (his = histidinate) is hydrolytically sensitive; the same holds for the related $[ReOCl_2(L\text{-}his)]$ species.[18] However, since (3+2)-type oxidorhenium(V) complexes with the tridentate trispyrazolylborate (tpb) ligand and a bidentate diolato ligand showed enhanced stability in aqueous solution, we felt encouraged to construct the ligand sphere about an oxidorhenium(V) core by an amino-acid–carbohydrate couple.[19] As a result, we report herein the synthesis and characterisation of two oxidorhenium(V) complexes with a L-histidinate–glycopyranoside couple which showed a prolonged lifetime in aqueous solutions of the physiological pH value.‡

The title compounds were prepared by refluxing the rhenium(V) precursor [$ReOCl_3(PPh_3)_2$], L-histidine, the glycoside and triethylamine in methanol in a molar ratio of 1:1:2:3. Full characterisation including a crystal-structure analysis succeeded for methyl α-D-mannopyranoside (Me-α-D-Man*p*) and methyl β-D-ribopyranoside (Me-β-D-Rib*p*) as the glycoside. The dianion of methyl α-D-mannopyranoside is a potential bidentate chelator by means of either its 2,3-*cis*-, 3,4-*trans*-, or 4,6-diol function. The known preference of the rhenium(V) central atom, which binds to the only *cis*-diolate function of methyl β-D-galactopyranoside in the tpb complex, made us expect to find the mannoside 2,3-bonded to the oxidorhenium(V) core as depicted in Scheme 1 (top).[19] In fact, the analysis of blue crystals of [ReO(L-his)(Me-α-D-Man*p*2,3H_{-2})]·2MeOH (**1**) that were crystallized from an aqueous extract of the reaction mixture, showed the attempted complex (Fig. 1).

The histidinato ligand is in a tridentate κ*N*,*N*,*O* binding mode with the carboxylato function *trans* to the oxido ligand. The ReO(his) part of the molecule completely resembles the structure

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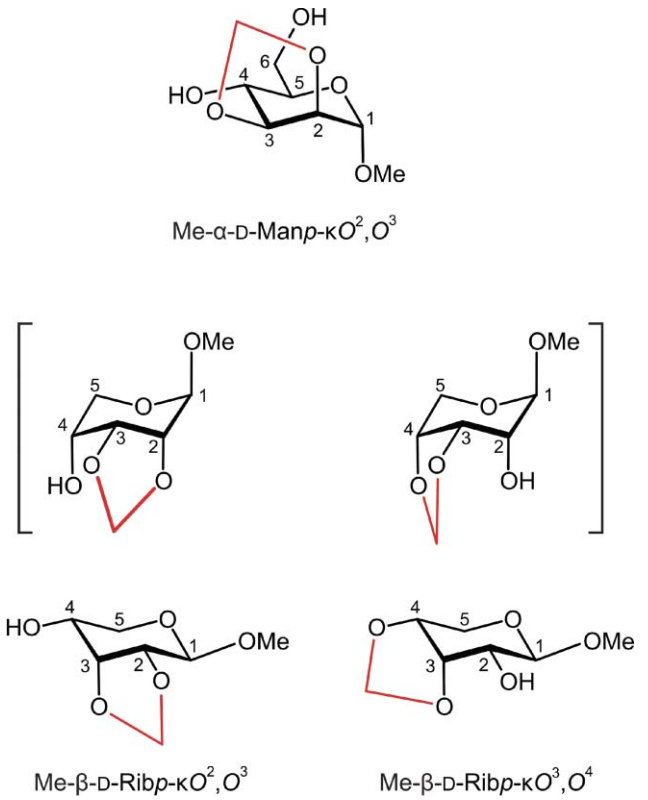


Scheme 1 The potential bidentate *cis*-diolate sites of the glycosides' dianions of this work. Top: methyl α-D-mannopyranoside. Middle and bottom: methyl-β-D-ribopyranoside; middle: the $^{1}C_{4}$ conformers that are found for the free glycoside; bottom: the $^{4}C_{1}$ conformers as found bonded to the oxidorhenium(V) core.

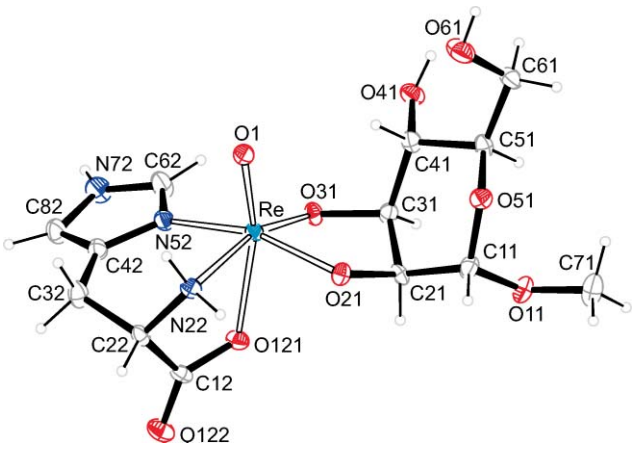


Fig. 1 The molecular structure of [ReO(L-his)(Me-α-D-Man*p*2,3H$_{-2}$)] in crystals of **1** (50% probability ellipsoids, methanol omitted). Distances [Å] and angles [°]: from Re to: O1 1.688(3), O21 1.955(2), O31 1.937(3), O121 2.183(3), N22 2.179(4), N52 2.098(3); O1–Re–O21 106.12(14), O1–Re–O31 107.62(13), O1–Re-O121 161.78(14), O1-Re-N22 91.62(14), O1-Re-N52 95.20(13), O21-Re-O31 82.75(10), O121-Re-N22 71.58(13), O121-Re-N52 78.17(11), N22-Re-N52 89.75(12), diol torsion angle O21-C21-C31-O31: –40.8(5), pyranose puckering parameters:[25] $Q = 0.527(5)$ Å, $\theta = 14.4(5)°$, $\varphi = 319(2)°$, conformation of the pyranose ring close to $^{4}C_{1}$.

reported by Beauchamp for the same fragment in [ReOCl$_2$(L-his)].[18] The *cis*-chlorido ligands of the latter are replaced by the 2,3-chelating dianion of methyl α-D-mannopyranoside. The mannoside is in *syn* orientation to the oxido ligand. In terms of the chelating diol function, the glycoside is distorted to some extent on binding to the central atom: compare its torsion angle in **1** of about –41° with the same angle of the free form (–55.5°).[20]

In contrast to the mannoside, methyl β-D-ribopyranoside (Me-β-D-Rib*p*) is a potentially chelating ligand with two *cis*-vicinal diol binding sites (O-2/3 and O-3/4). Moreover, two conformations appear as possible bidentate chelators (Scheme 1). The reaction of the pyranoside with [ReOCl$_3$(PPh$_3$)$_2$], L-histidine and triethylamine in methanol gave a blue solid from which crystals of [ReO(L-his)(Me-β-D-Rib*p*3,4H$_{-2}$)]·$\frac{1}{2}$MeOH (**2**) were grown after re-dissolution in a methanol/water mixture. The asymmetric unit of the crystals of **2** contains one molecule of the rhenium complex (Fig. 2) and a half-occupied methanol site. The dianion of methyl β-D-ribopyranoside is κO^3,O^4-bonded. The glycoside's orientation is, again, *syn* to the oxido ligand. The diol's torsion angle O3-C3-C4-O4 changes greatly from the free glycoside's value of –61.4(2)° to about 41° on coordination, since the conformation in the bonded state ($^{4}C_{1}$) is not the same as that found in the free glycoside ($^{1}C_{4}$).[21]

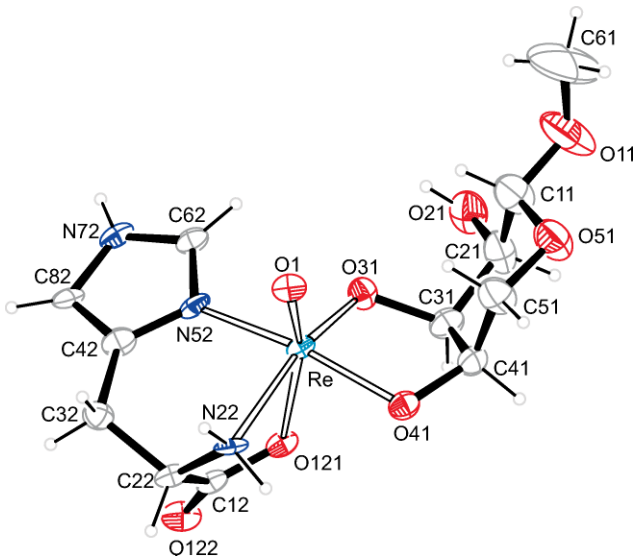


Fig. 2 The molecular structure of [ReO(L-his)(Me-β-D-Rib*p*3,4H$_{-2}$)] in crystals of **2** (40% probability ellipsoids, methanol omitted). Distances [Å] and angles [°]: from Re to: O1 1.684(7), O31 1.926(6), O41 1.960(5), O121 2.194(5), N22 2.179(6), N52 2.115(7); O1–Re–O31 111.6(3), O1–Re–O41 104.5(3), O1–Re–O121 162.5(3), O1-Re-N22 92.6(4), O1-Re-N52 96.7(4), O31-Re-O41 82.8(2), O121-Re-N22 71.0(4), O121-Re-N52 77.8(4), N22-Re-N52 90.5(3), diol torsion angle O31-C31-C41-O41: 41.3(10), pyranose puckering parameters:[25] $Q = 0.554(14)$ Å, $\theta = 17.9(13)°$, $\varphi = 35(5)°$, pyranose conformation close to $^{4}C_{1}$.

An NMR study showed that the crystallised species were not the only isomeric forms in the solution state. The ^{13}C NMR spectra of redissolved crystals of **1** in D$_2$O thus showed two signal sets of different intensities (Tables 1 and 2). Essentially the same distribution of product species was observed in spectra of the crude reaction mixtures in addition to the signals of residual starting materials and side products. The typical 'coordination-induced shifts' (CISs, see Tables 1 and 2) showed the κO^2,O^3 bonding

Table 1 $^{13}C\{^1H\}$ NMR chemical shifts (in ppm) of the L-histidinato ligands in D_2O. The coordination-induced shift (CIS, in ppm) is calculated as $\delta_{complex} - \delta_{free\ ligand}$ ($\Delta\delta$). For atomic numbering see Scheme 2. The methanol signal ($\delta = 49.50$ ppm in D_2O) was used as an internal secondary reference for the chemical shift.[22] Assignment of the free L-histidine according to the literature[23]

		COO^-	C_α	C_β	C2′	C4′	C5′
free L-hisH[a]	δ	174.4	55.5	28.9	136.9	132.9	117.4
1a	δ	180.3	59.5	27.9	145.6	138.6	117.9
	Δδ	5.9	4.0	–0.9	8.7	5.7	0.5
1b	δ	180.9	59.5	27.9	145.2	138.7	117.9
	Δδ	6.5	4.0	–0.9	8.3	5.8	0.5
free L-hisH[b]	δ	174.6	56.7	28.9	137.0	132.9	117.4
2a	δ	180.4	58.7	27.7	145.1	138.5	118.1
	Δδ	5.8	2.0	–1.2	8.1	5.6	0.7
2b	δ	180.4	59.3	28.0	145.6	138.8	118.1
	Δδ	5.8	2.6	–0.9	8.6	5.9	0.7
2c	δ	180.6	58.8	27.8	144.7	138.9	118.2
	Δδ	6.0	2.1	–1.1	7.7	6.0	0.8
2d	δ	180.5	58.8	27.9	145.8	138.6	117.9
	Δδ	5.9	2.1	–1.0	8.8	5.7	0.5

[a] pH 3.2. [b] pH 6.6; intensities: a > b (> c > d).

Table 2 $^{13}C\{^1H\}$ NMR chemical shifts (in ppm) of the pyranoside ligands in D_2O. The coordination-induced shift (CIS, in ppm) is calculated as $\delta_{complex} - \delta_{free\ ligand}$ ($\Delta\delta$). For atomic numbering see Scheme 1. The methanol signal ($\delta = 49.50$ ppm in D_2O) was used as an internal secondary reference for the chemical shift.[22] Assignment of the free pyranosides according to the literature.[24] CIS values at metal-binding positions are typed boldface

		C1	C2	C3	C4	C5	C6	OMe
Me-α-D-Man*p*	δ	101.5	70.6	71.3	67.4	73.2	61.6	55.3
1a	δ	101.6	90.5	91.0	68.3	71.8	61.7	55.5
	Δδ	0.1	**19.9**	**19.7**	0.9	–1.4	0.1	0.2
1b	δ	101.6	91.6	94.8	68.1	72.3	61.7	55.5
	Δδ	0.1	**21.0**	**23.5**	0.7	–0.9	0.1	0.2
Me-β-D-Rib*p*	δ	102.0	70.8	68.4	68.3	63.7		55.5
2a	δ	102.4	93.3	85.7	67.2	64.8		57.2
	Δδ	0.4	**25.5**	**17.3**	–1.1	1.1		1.7
2b	δ	102.1	71.4	90.4	93.7	64.0		57.6
	Δδ	0.1	0.6	**22.0**	**25.4**	0.3		2.1
2c	δ	102.5	94.1	88.6	67.6	63.7		57.5
	Δδ	0.5	**23.3**	**20.2**	–0.7	0.0		2.0
2d	δ	103.0	70.2	89.1	90.6	64.2		57.3
	Δδ	1.0	–0.5	**20.7**	**22.3**	0.5		1.8

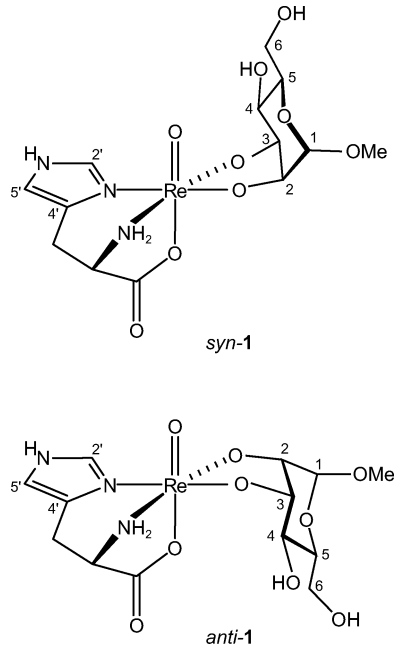
Intensities: a > b (> c > d).

mode for both species, thus demonstrating the preference of *cis*-vicinal diol functions for the coordination to the oxidorhenium(V) core. The existence of two solution species is indicative of *syn*/*anti* isomerism, the pyranoside's two possible orientations with respect to the oxido ligand (Scheme 2). In view of the result of the structure determination, the *syn*-isomer **1** is assumed to be the major solution species.

The situation is more complicated for methyl β-D-ribopyranoside. The structure determination shows that the glycoside is bonded to the central metal not before ring inversion. Accordingly, the spectral data available do not give a hint that the conformation of the free glycoside did occur in any of the solution species. Of these, a total of four make up the ^{13}C NMR spectra—both of the crude reaction mixtures and solutions of redissolved crystals. We concluded from this observation that the species equilibrate in the course of minutes though they show well-resolved signals and thus are inert on the NMR time scale. Combining the arguments—the *cis*-diol preference, the lack of the $^1C_4$ conformer, and the observation that the mannoside forms *syn*/*anti* isomers—the four signal sets indicate the presence of the two $^4C_1$ ligands of the bottom part of Scheme 1, each forming a *syn*/*anti* pair with the oxidorhenium(V) core.

Bond-breaking and -making in the course of the isomerisation reactions and the simultaneous lack of hydrolytical sensitivity suggest that the title compounds are not only inert against hydrolysis, but stable. This assumption is confirmed by the observation that aqueous solutions that contain the rhenium(V) complexes are accessible by an alternative route which is, moreover, more relevant for an attempted application than the above-described route that provides the pure substances. Thus, an almost neutral aqueous solution of perrhenate, histidine and the glycoside turns blue on reaction with a stannous oxalate suspension. ^{13}C NMR spectra of these solutions show the same isomer distribution of the title complexes as described above.

In conclusion, the combination of two types of biomolecules, an amino acid and a carbohydrate, results in the formation of oxidorhenium(V) species which are hydrolytically stable at the physiological pH value over weeks. An extension of this work, which was intended as a proof of principle and thus uses simple ligands that do not provide remote functions for



Scheme 2 Solution species of **1**: top: the tentative major *syn* species (*ca.* 2 parts of 3) that formed the crystals, bottom: the tentative minor *anti* isomer (*ca.* 1 part of 3).

bioconjugate formation, towards more complex glycosides and glycoses as well as to peptides, may contribute to diversify the currently investigated bifunctional-ligand strategy. Thus, the combination of underivatised functional groups of extended biomolecules simplifies this strategy. Moreover, the use of high-valent rhenium with its total of five points for ligand attack broadens the basis for drug design—in particular by the concurrent use of such diversified ligand classes as the peptides and the carbohydrates.

Notes and references

‡ The oxidorhenium(V) precursor $[ReOCl_3(PPh_3)_2]$ was prepared following a published procedure.[26] The general procedure for the preparation of the rhenium(V) complexes in methanol was done in analogy to known syntheses for mixed-ligand complexes with rhenium(V).[27,28] [ReO(L-his)(Me-α-D-Man*p*2,3H$_{-2}$)]·2MeOH (**1**) was prepared by stirring a suspension of $[ReOCl_3(PPh_3)_2]$ (833 mg, 1.0 mmol), L-histidine (155 mg, 1.00 mmol), methyl α-D-mannopyranoside (388 mg, 2.00 mmol) and triethylamine (303 mg, 3.00 mmol) under reflux in methanol (250 mL). After heating for 2 h to 50 °C, the yellow suspension turned into a blue solution. The volume was reduced *in vacuo* to 30 mL. The blue powder of **1** was filtered off and recrystallized from methanol. Yield: 340 mg, 62%. MS (FAB$^+$, glycerol) *m*/*z* calcd. for $C_{13}H_{21}N_3O_9Re$ [M + H]$^+$ 550.1, measured 550.4 with a characteristic Re_1 pattern. Elemental analysis calcd. for $C_{14}H_{24}N_3O_{10}Re$ [M + MeOH] C 28.96, H 4.17, N 7.24; found C 29.13, H 4.23, N 7.46. Crystal-structure analysis on **1**: $C_{15}H_{28}N_3O_{11}Re$, M_r = 612.60 g mol^{-1}, crystal size: 0.13 × 0.11 × 0.05 mm, T = 200(2) K, KappaCCD diffractometer, monoclinic, $C2$, a = 25.2622(4), b = 9.0735(2), c = 10.4724(2) Å, β = 114.2054(9)°, V = 2189.40(7) Å^3, Z = 4, μ = 5.610 mm^{-1}, numerical absorption correction (T range: 0.485–0.771), 19131 refls., R_{int} = 0.0367, mean σ(I)/I = 0.0372, θ range: 3.3–27.5°, Flack parameter: –0.021(7), 4946 refls. in refinement, 279 parameters, 1 restraint, $R(F_{obs})$ = 0.0207, $R_w(F^2)$ = 0.0486, S = 1.106, shift/error$_{max}$ < 0.001, max./min. residual density: –0.794/1.167 e Å^{-3}. In a similar procedure as in **1**, [ReO(L-his)(Me-β-D-Rib*p*3,4H$_{-2}$)]·0.5MeOH (**2**) was prepared by using methyl β-D-ribopyranoside (328 mg, 2.00 mmol) in 100 mL methanol. After 3 h at 60 °C the yellow suspension turned into a blue solution. The solvent was removed *in vacuo* and the remaining blue solid was recrystallized from a mixture of methanol (10 mL) and water (1 mL). Blue crystals of **2** formed within three days at room temperature. Yield: 21 mg, 4%. MS (FAB$^+$, NBA) *m*/*z* calcd. for $C_{12}H_{19}N_3O_8Re$ [M + H]$^+$ 520.1, measured 520.3 with a characteristic Re_1 pattern. Elemental analysis calcd. for $C_{12}H_{22}N_3O_{10}Re$ [M + 2 H_2O] C 25.99, H 4.00, N 7.58; found C 26.02, H 4.01, N 7.61. Crystal-structure analysis on **2**: the crystal-structure determination of **2** was hampered by stacking faults of the crystals. As a result, residual densities of up to about 6 e Å^{-3} were found in a difference-Fourier map at a distance of 3 Å from the rhenium atom. These densities were refined as rhenium atoms, the occupancy factors taking on values of maximally 0.02. Accordingly, the major rhenium position refined to 0.96. The 3-Å distance is in agreement with the assumption that the κO^2,O^3 isomer replaced some of the major isomer in the crystals of **2**. $C_{25}H_{40}N_6O_{17}Re_2$, M_r = 534.52 g mol^{-1}, crystal size: 0.18 × 0.13 × 0.02 mm, monoclinic, $P2_1$, a = 10.3763(3), b = 6.4665(2), c = 14.8657(5) Å, β = 96.001(2)°, V = 992.00(5) Å^3, Z = 2, μ = 6.168 mm^{-1}, numerical absorption correction (T range: 0.586–0.884), 17624 refls., R_{int} = 0.0504, mean σ(I)/I = 0.0477, θ range: 3.2–27.5°, Flack parameter: 0.041(14), 4484 refls. in refinement, 234 parameters, 1 restraint, $R(F_{obs})$ = 0.0389, $R_w(F^2)$ = 0.0879, S = 1.108, shift/error$_{max}$ < 0.001, max./min. residual density: 1.542/–1.782 e Å^{-3}. CCDC 737570 (**1**) and 737571 (**2**) contain the supplementary crystallographic data.‡

A route starting from ReO_4^- yielded the same rhenium-containing products in terms of NMR spectroscopy: ammonium perrhenate (268 mg, 1.00 mmol), L-histidine (155 mg, 1.00 mmol) and the methyl D-pyranoside (β-riboside: 328 mg, α-mannoside: 388 mg; 2.00 mmol) were dissolved in water (5 mL). A suspension of tin(II) oxalate (414 mg, 2.00 mmol) in water (5 mL) was added. Sodium hydrogen carbonate (168 mg, 2.00 mmol) was added to adjust the pH value to 8. After stirring for four hours, the suspension was filtered to obtain a blue solution (pH about 5). Re-adjustment of the pH value to 8 did not alter the solutions in terms of either visual inspection or NMR spectroscopy.

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