Nitrosyl Ruthenium Diolato Complexes[‡]

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Keywords: Ruthenium / Nitrosyl / Diols / Carbohydrate complexes

[*mer*-(dien)(NO)Ru(AnErytH$_{-2}$)]BPh_4·2H_2O (**1**), [*mer*-(dien)(NO)Ru(*R*,*R*-ChxdH$_{-2}$)]BPh_4 (**2**), [*mer*-(dien)(NO)Ru(EthdH$_{-2}$)]BPh_4 (**3**), and [*mer*-(dien)(NO)Ru(Me-β-D-Rib*f*2,3H$_{-2}$)]BPh_4·5.5H_2O (**4**) have been synthesized in the form of light pink crystals by the reaction of [*mer*-(dien)(NO)$RuCl_2$]X with the respective diol in aqueous sodium hydroxide solution (dien = diethylenetriamine, AnEryt = anhydroerythritol, Chxd = cyclohexane-1,2-diol, Ethd = ethanediol, Rib = ribose; X = BPh_4 or PF_6). The nitrosyl ligand exhibits a strong *trans* influence which causes the *trans*-bonded oxygen atom of the diolato ligand to form a shorter bond with the Ru centre. Mean values are 2.038 for *cis* and 1.946 Å for *trans* *O*-binding. Back donation is strongly supported by the diolato ligand resulting in low energies for the N–O stretch which can be observed as low as 1805 cm^{-1}. *trans*-Oxygen atoms do not act as hydrogen-bond acceptors in any of the cases.

Introduction

Ruthenium and its compounds are a class of particularly significant catalytically active materials. Carbohydrates on the other hand provide a biogenic, renewable feedstock which, however, is burdened with the problem of "overfunctionalisation". This term emphasises the fact that it is not merely the number but the similarity of the functional groups which causes problems with regioselectivity. Problems of this kind are typically solved in chemistry by means of catalysis. Bearing in mind the aims of the currently topical green chemistry, which promotes both catalytic reactions and the use of renewable resources, it is surprising that there is no structural information on the interaction of ruthenium centres and carbohydrates. This statement holds not only for monosaccharides but also for simple diols which provide the basic functional group of carbohydrates for metal chelation. This paper reports the synthesis and structural characterisation of the first diolato-ruthenium complexes in both the solid-state and solution. As starting materials, we used aqueous solutions of *trans*-dichloro-*mer*-diethylenetriamine-nitrosyl ruthenium(III) salts[1] which contain a nitrosyl ligand linearly bonded to the ruthenium centre thus forming the well-known, tricationic $\{RuNO\}^6$ fragment (for the Enemark–Feltham notation cf. ref.[2]). In the context of the hormonal action of nitrous oxide, the chemistry[3] of $\{RuNO\}^6$-type complexes has recently attracted interest in its own right due to the physiological activity of these species.[4,5]

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Results and Discussion

Synthesis of Crystalline [*mer*-(dien)(NO)Ru(DiolH$_{-2}$)] Tetraphenylborates

[*mer*-(dien)(NO)$RuCl_2$]BPh_4 reacts with anhydroerythritol (*cis*-oxolane-3,4-diol, AnEryt) in aqueous alkaline solution over the course of 2 h at 70 °C to yield the tetraphenylborate salt of the complex cation [*mer*-(dien)(NO)Ru(AnErytH$_{-2}$)]$^+$ without concomitant removal of the chloro ligands by special reagents such as silver oxide (method 1 in the Experimental Section). The application of slightly harsher reaction conditions allowed the synthesis of the same product to be initiated directly from nitrosyl-ruthenium chloride, diethylenetriamine and anhydroerythritol (method 2 in the Experimental Section). Method 1 achieved completion as judged by NMR spectroscopy. The precipitate was of a colour similar to the crystals. Method 2, however, results in a more or less brown precipitate which clearly contains by-products. Structural analyses using light pink crystals of the products from both methods revealed the formula [*mer*-(dien)(NO)Ru(AnErytH$_{-2}$)]BPh_4·2H_2O (**1**). Complexes of less acidic diols have been prepared with (*R*,*R*)-cyclohexane-1,2-diol [(*R*,*R*)-Chxd] and ethane-1,2-diol (Ethd). Both diols are less reactive than oxolanediol in terms of the diol remaining uncoordinated after the reaction with the ruthenium starting material in an approximately equimolar ratio according to method 1. Hence, about half of the cyclohexanediol and about one fifth of the ethanediol react in this experimental setup. Crystallisation achieved according to the procedures given in the Experimental Section yielded solvent-free crystals containing the attempted diolato complexes with the formulae [*mer*-(dien)(NO)Ru(*R*,*R*-ChxdH$_{-2}$)]BPh_4 (**2**) and [*mer*-(dien)-(NO)Ru(EthdH$_{-2}$)]BPh_4 (**3**). Attempts to include a carbo-

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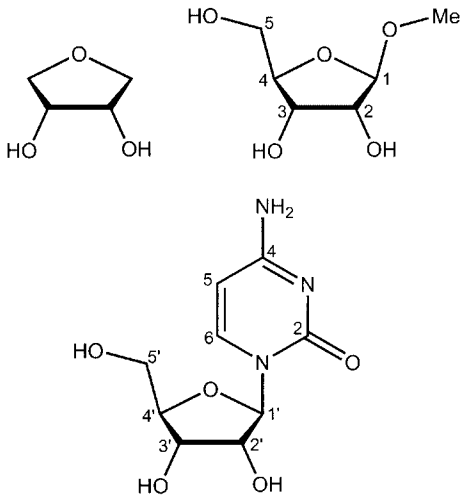
hydrate derivative were successful for methyl-β-D-ribofuranoside which contains the anhydroerythritol core (Scheme 1). Here, red crystals of [*mer*-(dien)(NO)Ru(Me-β-D-Rib*f*2,3H$_{-2}$)]BPh_4·5.5H_2O (**4**) were obtained by applying method 2.



Scheme 1.

The Diolato-{RuNO}^{6} Moiety

The structures of the four complex cations (**1**: Figure 1, **2**: Figure 2, **3**: Figure 3, **4**: Figures 4 and 5) reveal dianionic diolato(2–) ligands bonded to an octahedrally coordinated ruthenium centre. Isomerisation occurred during the course of the reaction: in the starting complex, one nitrogen atom of the dien ligand is *trans* to the nitrosyl group, whereas in the product, all three nitrogen atoms of the *mer*-dien ligand are bonded *cis* to the NO.

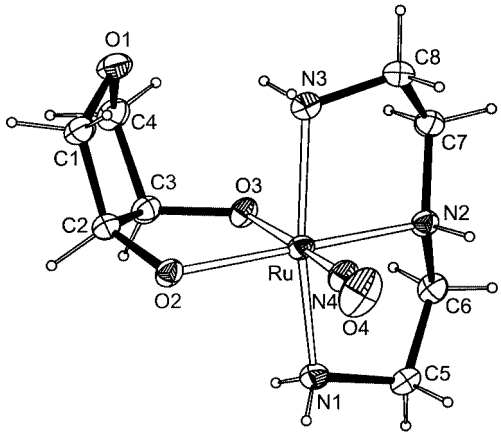


Figure 1. The structure of the [(*mer*-dien)(NO)Ru(AnErytH$_{-2}$)]$^+$ cation in **1**. Distances [Å] and angles [°]: from Ru to: N4 1.746(2), O3 1.940(2), O2 2.046(2), N2 2.070(2), N1 2.108(2), N3 2.112(2); O1–C1 1.443(3), O1–C4 1.443(3), O2–C2 1.416(3), O3–C3 1.432(3), C1–C2 1.540(3), C2–C3 1.542(4), C3–C4 1.518(4); O3–Ru–O2 81.80(7), C2–O2–Ru 112.13(14), C3–O3–Ru 117.92(14), O4–N4–Ru 171.0(2); O2–C2–C3–O3 –22.1(3).

Diolate–RuNO bonding is governed by the *trans*-influence of the nitrosyl ligand. Mean values for significant

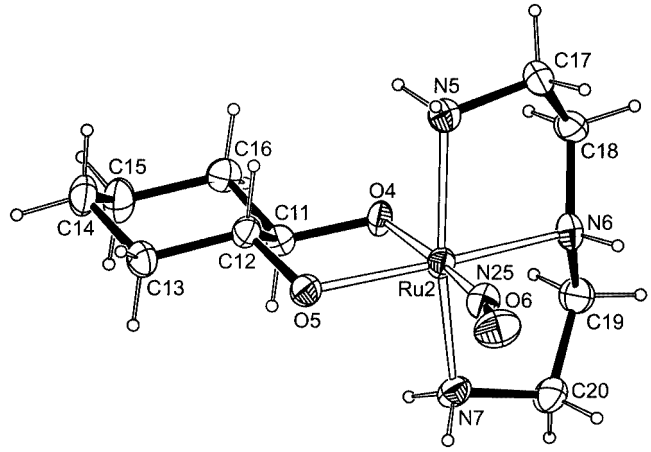


Figure 2. The structure of one of two symmetry-independent [*mer*-(dien)(NO)Ru(*R*,*R*-ChxdH$_{-2}$)]$^+$ cations in **2**. Distances [Å] and angles [°]: from Ru1 to: N4 1.752(5), O2 1.946(4), O1 2.046(4), N2 2.070(4), N3 2.086(5), N1 2.108(5); O1–C1 1.424(6), O2–C2 1.425(5), O3–N4 1.177(6), C1–C2 1.492(6); from Ru2 to: N25 1.725(5), O4 1.955(4), O5 2.041(4), N6 2.090(4), N7 2.091(5), N5 2.126(5); O4–C11 1.439(5), O5–C12 1.426(6), O6–N25 1.161(6), C11–C12 1.516(6); O2–Ru1–O1 82.51(15), C1–O1–Ru1 110.1(3), C2–O2–Ru1 110.4(3), O3–N4–Ru1 169.3(4), O4–Ru2–O5 83.76(15), C11–O4–Ru2 111.4(3), C12–O5–Ru2 106.2(3), O6–N25–Ru2 169.5(5); O1–C1–C2–O2 –49.6(4), O4–C11–C12–O5 –53.4(4).

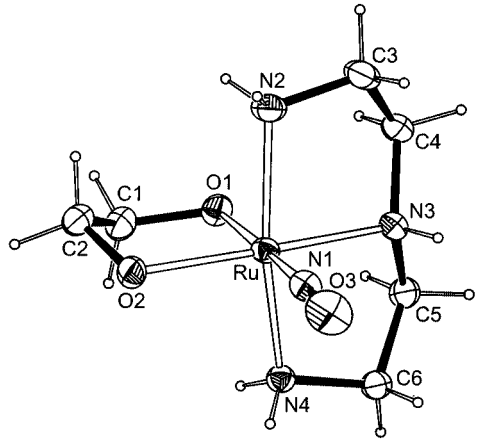


Figure 3. The structure of the [(*mer*-dien)(NO)Ru(EthdH$_{-2}$)]$^+$ cation in **3**. Distances [Å] and angles [°]: from Ru to: N1 1.743(3), O1 1.945(2), O2 2.029(2), N3 2.086(3), N4 2.090(3), N2 2.127(3); O2–C2 1.404(4), O1–C1 1.427(4), O3–N1 1.157(4), C1–C2 1.511(5); O1–Ru–O2 82.50(10), C2–O2–Ru 109.1(2), C1–O1–Ru 113.7(2), O3–N1–Ru 176.8(3); O1–C1–C2–O2 –45.4(4).

parameters have been listed in Table 1. There are some features common to **1**–**4**: (1) the Ru–O(*trans*) distance is always markedly shortened compared with the Ru–O(*cis*) distance, (2) the Ru–O(*trans*)–C angle is always more obtuse than the Ru–O(*cis*)–C angle and, most remarkably, considering the usual features of polyolato-metal structures, (3) the O(*trans*) centre does not act as a hydrogen-bond acceptor in any of the structures. On the other hand, O(*cis*) is a hydrogen-bond acceptor, as is usual.

The energies for the N–O stretching vibration are rather low, the minimum being 1805 cm^{-1} for **2** (cf. 1889 cm^{-1} for the starting material complex [*mer*-(dien)(NO)RuCl_2]BPh_4

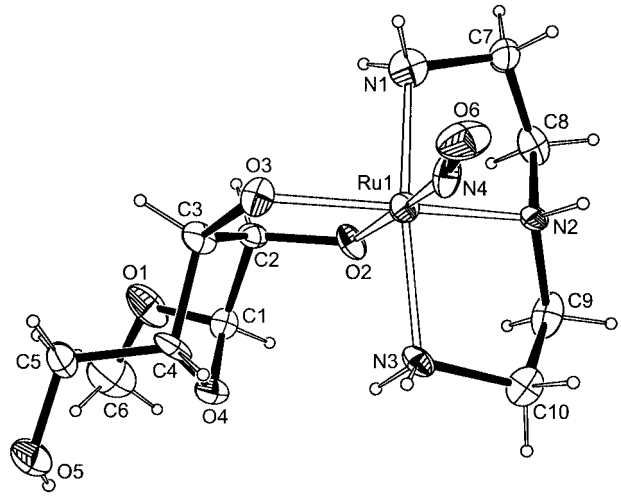


Figure 4. The structure of the O2(*trans*) isomer of the [(*mer*-dien)(NO)Ru(Me-d-Rib*f*2,3H$_{-2}$)]$^+$ cation in **4**. Distances [Å] and angles [°]: from Ru1 to: N4 1.740(9), O2 1.961(6), N2 2.052(8), O3 2.054(6), N1 2.098(9), N3 2.113(8); N4–O6 1.170(10); O2–Ru1–O3 82.2(3), O6–N4–Ru1 168.6(7), C3–O3–Ru1 113.4(6), C2–O2–Ru1 116.8(5); O2–C2–C3–O3 29.1(11).

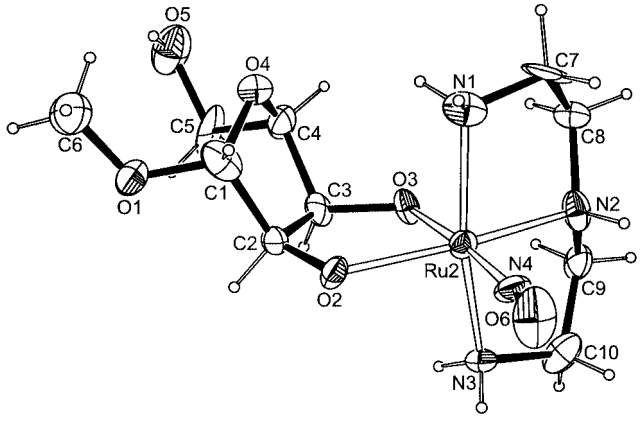


Figure 5. The structure of the O3(*trans*) isomer of the [(*mer*-dien)(NO)Ru(Me-d-Rib*f*2,3H$_{-2}$)]$^+$ cation in **4**. Distances [Å] and angles [°] (add the digit "1" to the labels of the C, N, and O atoms to extract more values from the Crystallographic Information File) from Ru2 to: N4 1.759(9), O3 1.914(6), O2 2.065(6), N2 2.067(8), N3 2.100(9), N1 2.107(8); N4–O6 1.151(10); O3–Ru2–O2 82.6(3), O6–N4–Ru2 169.9(8), C3–O3–Ru2 118.6(6), C2–O2–Ru2 112.7(6); O2–C2–C3–O3 –8.5(12).

with a *trans*-Cl–Ru–NO moiety). Such low values may be expected for *trans* ligands which effectively support electron density donation into the NO π* orbital. Hence, it is not surprising that both the geometric and spectroscopic parameters of **1**–**4** resemble three closely related methoxo and ethoxo complexes which have been reported very recently by Nagoa et al.[6,7] Using pyridine-2-carboxylate (pyca) groups as coligands, these authors reported structural and spectroscopic data for *cis*-[6] and *trans*-[Ru(NO)(OMe)(pyca)$_2$],[7] *cis* and *trans* referring to the orientation of the NO group and the methoxo ligand. These data have been added to Table 1 for comparison. In addition, IR data have been reported on the ethoxo homologue[6] which shares, with our diolates, a low value for the NO stretch of 1815 cm^{-1}. It should be noted that the rules derived by Nagoa et al. regarding the stability of isomers at the {RuNO}^{6} centre are supported by our data. According to these rules, isomers with one of the dien-nitrogen atoms *trans* to the nitrosyl group should be less stable than the species which have been isolated. The number of isomers is thus limited. Due to the equivalence of the hydroxy groups of the parent diols of **1**–**3**, only one isomer can be expected for a diolato complex. In fact, only one ^{13}C signal can be observed for each carbon atom which is part of a ruthenium complex in each of the respective reaction mixtures.

NMR Spectroscopy

One of the reasons for starting the investigation of ruthenium-carbohydrate interactions with {RuNO}^{6} complexes is because of their diamagnetism which enables monitoring of the progress of polyolate binding to the ruthenium centre by NMR spectroscopy. ^{13}C NMR spectra of solutions of **1**–**4** in fact show a marked "coordination-induced shift" (CIS) – a typical down-field shift of the signals of the diol carbon atoms which bear metal-binding oxygens. In addition, the kinetic inertness of the starting material and the product ruthenium complexes is the reason why the signals of metal-bonded and nonbonded diols occur separately in the spectra. This includes the NMR behaviour of possible coordination isomers which, however, are missing for **1**–**3** due to the reasons discussed in the previous paragraph. CIS values are best taken from the spectra of the aqueous reaction mixtures since they contain both the signals of the complex and the free diol (DMSO spectra of the pure products, which are given in the Experimental Section, do not

Table 1. Mean Ru–O distances [Å], Ru–O–C angles [°] and wave numbers ṽ [cm^{-1}] of the N–O stretching vibrations in **1**–**4** and in two isomers of [Ru(NO)(OMe)(pyca)$_2$] (**8**; pyca = pyridine-2-carboxylate).[6,7] *Cis* and *trans* refer to the configuration of NO and the respective diol or methoxo O atom.

	1	**2**	**3**	**4**	**8**
ṽ(NO)	1825	1805	1823	1819, 1838[a]	1838[b]
Ru–O(*trans*)	1.940	1.951	1.945	1.938	1.964[b]
Ru–O(*cis*)	2.046	2.044	2.029	2.060	2.040[c]
Ru–O(*trans*)–C	117.9	110.9	113.7	117.7	123.6[b]
Ru–O(*cis*)–C	112.1	108.2	109.1	113.1	116.2[c]

[a] Cf. Figure 7. [b] Values for the *trans* isomer according to ref.[7] [c] Values for the *cis* isomer according to ref.[6]

Table 2. ^{13}C NMR spectra of the crude reaction mixtures from which crystals of **4** were isolated (100.5 MHz, 25 °C). Atom numbering is defined in Scheme 1. $\Delta\delta$ values indicating a coordination-induced shift (CIS) are printed **boldface**.

		C1	C2	C3	C4	C5	C6
major isomer	δ/ppm	109.5	88.6	87.0	83.7	63.6	54.3
	$\Delta\delta$/ppm	2.0	**14.8**	**16.7**	1.1	1.3	0.0
minor isomer	δ/ppm	109.0	88.1	86.6	84.6	62.8	54.2
	$\Delta\delta$/ppm	1.5	**14.3**	**16.3**	2.0	0.5	–0.1
Me-β-D-Rib*f*	δ/ppm	107.5	73.8	70.3	82.6	62.3	54.3

Table 3. ^{13}C NMR spectra of the crude reaction mixtures of [*mer*-(dien)(NO)RuCl$_2$]PF$_6$ and cytidine at pH 12.5 (100.5 MHz, 25 °C). Atom numbering is defined in Scheme 1. $\Delta\delta$ values indicating a coordination-induced shift (CIS) are printed **boldface**.

		C1′	C2′	C3′	C4′	C5′	C2	C4	C5	C6
major isomer	δ/ppm	96.2	87.9	85.3	86.7	61.4	165.4	157.4	95.6	140.0
	$\Delta\delta$/ppm	6.6	**14.5**	**16.5**	3.5	1.1	–0.2	0.5	0.0	–1.0
minor isomer	δ/ppm	95.7	90.1	84.8	86.9	60.7	165.4	157.4	95.6	140.0
	$\Delta\delta$/ppm	6.1	**16.7**	**16.0**	3.7	0.4	–0.2	0.5	0.0	–1.0
Cytidine	δ/ppm	89.6	73.4	68.8	83.2	60.3	165.6	156.9	95.6	141.0

show the free diol signals. Hence, a less realistic reference state must be defined). CIS values range from ca. 8 to 15 ppm for **1**–**3** (**1**: 15.0, 13.7 for diol carbons; 3.4, 3.1 for carbons adjacent to the coordinating diol; **2**: 11.6, 9.1 and 1.3, 1.1 in addition to 0.3, 0.2 for the carbons most distant from Ru; **3**: 9.9, 8.1 ppm). For **4** and the related diol cytidine, the coordination induced shifts are slightly larger (Table 2 and Table 3). It is likely that a connection could be made between the differences in the diol CIS values (**1**: 1.3, **2**: 2.5, **3**: 1.7, **4**: 1.9, 2.0; cytidine: 0.7, 2.0) and *cis* and *trans* bonding to NO. However, no sound assignment is possible on the basis of the present data.

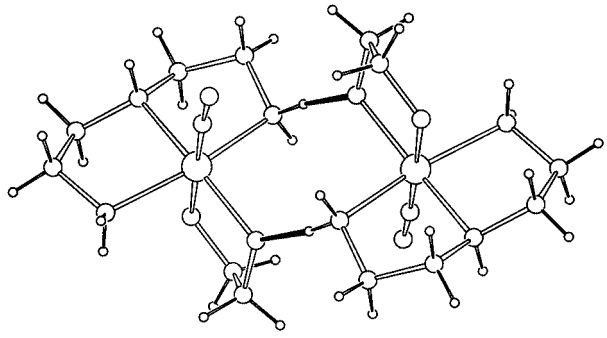


Figure 6. The C_i-symmetric dimer in crystals of **3**. The metric parameters of the hydrogen bond are: N4–H741 0.92, H···O2^{i} 1.76, N4···O2^{i} 2.672(3) Å, N4–H–O2^{i} 170°; symmetry code: ^{i} 1 – *x*, –*y*, –*z*. Similar, but C_1-symmetric dimers are present in the chiral crystals of **2** with the parameters: N3–H732 0.90, H···O5 1.84, N3···O5 2.729(6) Å, N3–H–O5 171°; N7–H771 0.90, H···O1 1.89, N7···O1 2.772(6) Å, N7–H–O1 165°.

Hydrogen Bonds

The individual crystal structures have some special features. Although crystallised from aqueous solution, crystals of **2** and **3** are anhydrous. Hence the N–H functions of the dien ligand are the only possible hydrogen-bond donors. In both structures, only one hydrogen bond is established towards each O(*cis*) acceptor but these bonds are unusually short when compared with N–H···O bonds usually found in polyolato-metal complexes – the shortest one having been observed in **3**: N···O2(*cis*) is 2.672(3) Å. Also, in both structures, two complex cations are linked by two such bonds to form a hydrogen-bonded dimer – a centrosymmetric dimer in **3** (Figure 6) and a similarly assembled dimer of the two symmetrically independent cations of the asymmetrical unit in crystals of the chiral complex **2**.

While there are dimers embedded in an assembly of the large tetraphenylborate counterions in **2** and **3**, the O(*cis*) atoms in **1** and **4** are hydrogen-bonded to water donors and, concomitantly, the complex cations form a structure with the counterions without having close contacts with one another. The structure determination for **1**, which was of a higher quality than that of **4**, reveals typical hydrogen-bonding parameters for the furanoidic ligand with the exception of the lack of such bonds towards the *trans*-oxygen (Table 4). It should be noted that the presence of additional hydrogen-bond acceptors (**1**) or donors and acceptors (**4**) is clearly not the reason for the presence or absence of water molecules in the crystals and the assembly of dimers and vice versa. Using *cis*-cyclopentane-1,2-diol (*cis*-Cptd), which parallels ethanediol and cyclohexanediol in being a simple diol without further functionality, a preliminary structure determination on centrosymmetric triclinic crystals of low quality revealed a hydrated product [*mer*-(dien)(NO)Ru(*cis*-CptdH$_{-2}$)]BPh$_4$·3H$_2$O (**5**). The structure of the complex cation follows the rules presented above. As in **1** and **4**, individual cations and not dimers are embedded in separated counterion surroundings.

Isomers in the Case of Glycoside and Nucleoside Ligation

As mentioned, the hydroxy groups of the diol functions of anhydroerythritol, (*R*,*R*)-cyclohexane-1,2-diol and ethane-1,2-diol are equivalent. Hence no isomers are formed upon rotating the diol functions at the ruthenium centre. The riboside ligand is different in this respect and two iso-

Table 4. Hydrogen bonds in **1** with distances [Å] and angles [°]. Note that O3 does not act as an acceptor (symmetry codes: [i]*x*, *y* – 1, *z*; [ii] 1 – *x*, –*y*, 1 – *z*; [iii] 1 – *x*, –1 – *y*, 1 – *z*).

D	H	A	D–H	H···A	D···A	D–H···A
O91	H911	O92[i]	0.89(4)	1.89(4)	2.769(3)	172(4)
O91	H912	O1	0.77(5)	2.19(5)	2.942(3)	165(4)
O92	H921	O2	0.80(4)	2.01(4)	2.777(3)	160(3)
O92	H922	O2[ii]	0.81(3)	1.92(3)	2.728(3)	171(3)
N1	H711	O92	0.86(3)	2.46(3)	3.115(3)	133(2)
N3	H731	O1	0.89(3)	2.30(3)	3.099(3)	150(2)
N3	H732	O91[iii]	0.85(3)	2.04(3)	2.874(3)	168(3)

mers can be expected – one in which O2 is the *trans*-oxygen and the other in which O3 occupies that position. Indeed, both isomers are present in crystals of **4**. Formation of the crystals was somewhat unusual. After a brown slurry had precipitated, crystals of **4** grew within this slurry over the course of three days, leaving part of the slurry unchanged. NMR spectra of the redissolved crystals showed the expected number of signals which is twice the number of carbon atoms of the riboside. NMR spectra of the brown residue obtained by washing, filtering and redissolving the slurry in dimethyl sulfoxide, clearly consist of only one half of the signals of the crystalline material. Obviously, the two isomers are not formed in equal amounts during the course of the reaction as expected but there is a main species. Crystallisation proceeds to the point where all of the minor species is spent, leaving the remaining major species in its finely divided state.

Due to the difference in back donation, parameters connected with the {RuNO}^{6} moiety should reflect whether O2 or the slightly more basic O3 atom is *trans* to the ruthenium centre. A measure of this difference is the energy of the N–O stretch. Actually, Figure 7 shows the absorption to be slightly split. Lorentz curve-fitting yields peak values of 1819 and 1838 cm^{-1}. Though the existence of two isomers has been demonstrated from X-ray work as well as NMR and IR spectroscopy, assignment of the spectroscopic data to an individual structure remains uncertain. If higher back donation is assigned to the more basic O3, the main species in the reaction mixture should, hence, be the O3(*trans*) isomer. It should be noted that the quality of the structure analysis did not produce sufficiently sound values for the bond lengths to contribute meaningfully to this study (cf. Experimental Section).

The related nucleosides react differently with the ruthenium starting material. No substantial shift in the ribose signals was observed for uridine and guanosine which bind to ruthenium through the uracil and guanidine residues, respectively. Note that both nucleosides can provide deprotonated amide functions which are obviously stronger ligands for ruthenium than a diolate. With cytidine, however, the ^{13}C NMR spectra closely resemble those of the methyl-β-D-ribofuranoside complexes (cf. the formulae in Scheme 1). The ratio of the major and minor isomers depends on the synthetic procedure chosen. When prepared as described in the Experimental Section by means of microwave heating, there is a distinct difference in the two isomers. Hence, assignment of the signals to one of the isomers is unambiguous. All attempts to crystallise one or both of the isomers have proved unsuccessful so far. The procedure given yielded small needles or platelets both of which were too weakly diffracting for structural analysis.

Conclusions

The {RuNO}^{6} moiety is a well-suited metal fragment for diolate binding. The diolato ligand markedly strengthens back-donation to the nitrosyl ligand. Hence, the energy values for the N–O stretching vibration slightly above 1800 cm^{-1} are at the lower end of those reported in the literature. The applied synthetic methods are suitable for the preparation of complexes of simple diols, nucleosides and other glycosides which are stable under more strongly alkaline conditions and at elevated temperatures. Work is in progress to prepare compounds of this type at conditions which are mild enough such that ruthenium complexes of monosaccharides can also be synthesized.

Experimental Section

trans-Dichloro-*mer*-diethylenetriamine-nitrosyl ruthenium(III) tetraphenylborate (**6**) and *trans*-dichloro-*mer*-diethylenetriamine-

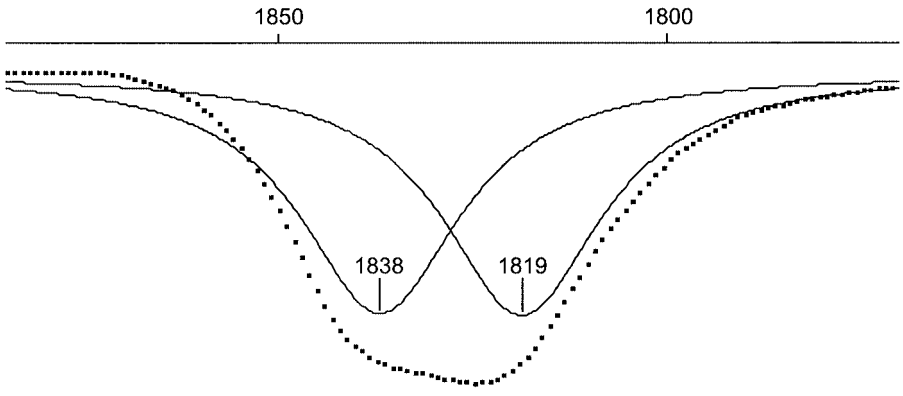


Figure 7. The baseline-corrected region of the N–O stretching vibration taken from crystalline samples of **4**. The numbers given are ṽ values in cm^{-1}.

nitrosyl ruthenium(III) hexafluorophosphate (**7**) were prepared according to the literature.[1] The results reported appear to be independent of the supplier of the diols, diethylenetriamine and the salts which provide the counterions. It should be noted, however, that the appearance of $Ru(NO)Cl_3 \cdot H_2O$ differs from one supplier to the other. For **1**, we used $Ru(NO)Cl_3 \cdot H_2O$ from Strem and anhydrous $Ru(NO)Cl_3$ from ABCR. For **4**, $Ru(NO)Cl_3 \cdot H_2O$ from Chempur was used.

For the reactions with cytidine a CEM Discover microwave oven was used.

$^{13}C\{^1H\}$ spectra were recorded using 1 mL of the appropriate filtered aqueous reaction mixture in a 5 mm tube. Reference signals of the free diols were subsequently recorded after addition of the respective diol to the measured reaction mixture. Equipment used: ^{13}C NMR spectroscopy: Jeol EX-400. Mass spectrometry: Jeol JMS-700 (ionisation method: FAB^+). IR spectroscopy: Nicolet 520-FTIR.

The equipment used for the structure determinations was an Enraf Nonius KappaCCD diffractometer in the case of **2**–**4** (rotating anode, 4.125 kW source power, Mo-K_α radiation, graphite monochromator) and a Stoe IPDS instrument (sealed tube, 2.75 kW source power, Mo-K_α radiation, graphite monochromator) for **1**. Crystallographic data are summarised in Table 5.

CCDC-226508 (for **1**), 226509 (for **2**), 226510 (for **3**) and 226511 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In the structure determination of **3**, a high residual density of 3.4 e Å^{-1} was calculated at a distance of 1.3 Å from Ru. The reason for this high value remains unclear and the next density was as low as 0.6 e Å^{-1}. The structure determination using a crystal of **4** was complicated by a considerable degree of pseudo-symmetry. Though being built up from a chiral motif, most atoms of the unit-cell keep to a centrosymmetric arrangement. Hence, most of the structure can be described in space group $P\bar{1}$ (instead of $P1$). The origin of the pseudosymmetry of the crystals is the pseudosymmetry of the methyl-β-D-ribofuranoside ligand. Taking the methoxy residue at C1 and the hydroxymethyl substituent at C4 as equivalent (Scheme 1), the riboside exhibits C_s symmetry. It is not usual for this pseudosymmetry to find itself expressed in a crystal structure since a hydroxymethyl residue, being a hydrogen-bond donor, is clearly different from the more hydrophobic methoxy group. However, in the structure of **4**, this rare case is realised and it interferes with the structure refinement.

***mer*-Diethylenetriamine-{*cis*-oxolane-2,3-diolato(2–)}-nitrosyl Ruthenium(III) Tetraphenylborate Dihydrate (1). Method 1:** Compound **6** (667 mg, 1.068 mmol) was dissolved in hot water (350 mL) with vigorous stirring. The pH value was adjusted to 12 by addition of 2 M sodium hydroxide. After addition of anhydroerythritol (111 mg, 1.068 mmol), the solution was heated to 70 °C for 2 h. Upon cooling, an orange-pink precipitate formed which was filtered off, washed with some water and dried under vacuum to yield ca.

Table 5. Crystallographic data.

	1	**2**	**3**	**4**
empirical formula	$C_{32}H_{43}BN_4O_6Ru$	$C_{34}H_{43}BN_4O_3Ru$	$C_{30}H_{37}BN_4O_3Ru$	$C_{34}H_{54}BN_4O_{11.5}Ru$
M_r [g mol^{-1}]	691.59	667.61	613.52	814.69
crystal size [mm]	0.29 × 0.19 × 0.15	0.16 × 0.12 × 0.08	0.32 × 0.18 × 0.16	0.35 × 0.18 × 0.15
T [K]	200(2)	293(2)	200(2)	200
diffractometer	Stoe IPDS	KappaCCD	KappaCCD	KappaCCD
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/n$	$P1$
a [Å]	9.2991(8)	11.59660(10)	12.50320(10)	10.6371(2)
b [Å]	10.4514(8)	12.68100(10)	17.6215(2)	11.4939(2)
c [Å]	17.3793(16)	22.8485(2)	12.9580(2)	17.0986(5)
α [°]	86.332(10)	90	90	73.2656(9)
β [°]	79.131(11)	102.1646(4)	92.4843(6)	89.3241(10)
γ [°]	72.835(10)	90	90	72.5096(9)
V [Å^3]	1584.8(2)	3284.57(5)	2852.29(6)	1903.01(8)
Z	2	4	4	2
calcd. density [g cm^{-3}]	1.44930(18)	1.35008(2)	1.42873(3)	1.42180(6)
μ [mm^{-1}]	0.545	0.516	0.588	0.456
absorption correction	numerical	numerical	numerical	none
transmission factor range	0.9242–0.9543	0.9925–0.9975	0.8163–0.9209	–
refls. measured	27826	51865	35849	21490
R_{int}	0.0583	0.0626	0.0425	0.0507
mean $\sigma(I)/I$	0.0586	0.0679	0.0263	0.0748
θ range	3.15–27.51	3.52–27.52	3.20–26.00	3.58–24.00
observed refls.	5915	11321	4936	9594
x,y (weighting Scheme)	0.0114, 0.9645	0.0274, 1.2099	0.0588, 6.2238	0.0345, 1.2526
Flack parameter	–	–0.04(3)	–	–0.02(3)
refls in refinement	7241	14614	5586	11425
parameters	530	775	353	995
restraints	0	1	0	36
$R(F_{obs})$	0.0364	0.0409	0.0432	0.0440
$R_w(F^2)$	0.0739	0.0895	0.1178	0.0986
S	1.042	1.052	1.035	1.022
shift/error$_{max}$	0.001	0.002	0.001	0.001
max. electron density [e Å^{-3}]	0.325	0.531	3.374	0.618
min. electron density [e Å^{-3}]	–0.627	–0.565	–0.565	–0.403

200 mg of a pink solid. Dissolving the solid in as small an amount of methanol as possible followed by slow evaporation of the solvent gave light pink crystals of **1**. Compound **1** is slightly soluble in water and ethanol and very soluble in methanol. $C_{32}H_{43}BN_4O_6Ru$ (691.59): calcd. C 55.6, H 6.3, B 1.56, N 8.1, Ru 14.6; found C 56.9, H 6.3, B 1.50, N 8.1, Ru 14.9. ^{13}C NMR (100 MHz, [D_6] DMSO): δ = 164.7–163.2 (4 signals, phenyl, C_{ipso}), 136.1 (phenyl, C_{ortho}), 125.9 (phenyl, C_{meta}), 122.1 (phenyl, C_{para}), 88.1, 87.8 (diol, 2H, CH), 77.1, 75.5 (diol, 2H, CH_2), 50.8, 50.4, 50.2, 49.8 (dien, 4H, CH_2) ppm. MS (FAB^+): *m*/*z* (%) = 337 (15) $[M + H]^+$, 336 (8) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1825 (vs, N–O), 1579 (vw), 1480 (w), 1453 (w), 1427 (w), 1119 (w), 1052 (sh), 1035 (m), 739 (st), 710 (st), 612 (m) cm^{-1}.

Method 2: Anhydrous nitrosyl-ruthenium(III) chloride (445 mg, 1.87 mmol) or the equivalent amount of nitrosyl-ruthenium(III) chloride monohydrate was dissolved in water (20 mL). The pH value was adjusted to 11 by addition of 2 M sodium hydroxide. A solution of diethylenetriamine (193 mg, 1.87 mmol) and anhydroerythritol (195 mg, 1.87 mmol) in water (5 mL) was added dropwise. The pH value was readjusted to 11 by addition of either 0.1 M hydrochloric acid or 0.1 M sodium hydroxide and the solution was then heated to reflux for 3 h. Excess sodium tetraphenylborate was then added to the hot solution. A pink to light-brown precipitate formed which was filtered off, washed with cold water and recrystallised from methanol to yield light pink crystals of **1**. Both methods yield ca. 10% of the crystalline product.

***mer*-Diethylenetriamine-{*R*,*R*-cyclohexane-1,2-diolato(2–)}-nitrosyl Ruthenium(III) Tetraphenylborate (2):** Compound **6** (580 mg, 0.929 mmol) was dissolved in water (300 mL). The pH value was adjusted to 13 with 2 M sodium hydroxide and (*R*,*R*)-cyclohexane-1,2-diol (324 mg, 2.79 mmol) was added. The resultant solution was heated to reflux at 80 °C for 2 h. After standing overnight, a mixture of yellow-pink crystals of **2** and colourless crystals of unreacted starting material were formed. Compound **2** is poorly soluble in water but freely soluble in methanol. $C_{34}H_{43}BN_4O_3Ru$ (667.61): calcd. C 61.2, H 6.5, B 1.62, N 8.4, Ru 15.1; found C 60.9, H 6.4, B 1.51, N 8.3, Ru 15.0. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 164.7–163.2 (4 signals, phenyl, C_{ipso}), 136.1 (phenyl, C_{ortho}), 125.9 (phenyl, C_{meta}), 122.1 (phenyl, C_{para}), 89.0, 88.5 (diol, 2 CH), 50.8, 50.4, 50.2, 49.8 (dien, 4 CH_2), 35.6, 34.9 (diol, 2 CH_2), 23.1 (diol, 2 isochronous CH_2); signals of the free diol in water: δ = 73.9 (2 CH; C1, C2), 31.5 (2 CH_2; C3, C6), 22.7 (2 CH_2; C4, C5) ppm. MS (FAB^+): *m*/*z* (%) = 349 (65) $[M + H]^+$, 348 (37) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1805 (vs, N–O), 1579 (m), 1568 (sh), 1480 (m), 1455 (m), 1427 (m), 1089 (m), 1071(m), 1034 (m), 739 (st), 709 (st), 641 (st), 610 (st) cm^{-1}.

***mer*-Diethylenetriamine-{1,2-ethanediolato(2–)}-nitrosyl Ruthenium(III) Tetraphenylborate (3):** Compound **7** (97 mg, 0.216 mmol) was dissolved in water (10 mL). 1,2-Ethanediol (11 mg, 0.216 mmol) was added, the pH value adjusted to 12.5 by addition of 2 M sodium hydroxide and the reaction mixture heated to 70 °C for 2 h. The cooled solution was then carefully layered with sodium tetraphenylborate solution (5 mL) which had been saturated at room temperature. Reddish-brown prisms of **3** crystallised overnight at the boundary between the layers. Solution behaviour resembles that of **2**. $C_{30}H_{37}BN_4O_3Ru$ (613.52): calcd. C 58.7, H 6.1, B 1.76, N 9.1, Ru 16.5; found C 58.7, H 6.1, B 1.56, N 8.9, Ru 16.3. ^{13}C NMR (100 MHz, H_2O): δ = 72.4, 74.2 (diol, 2 CH_2), 50.7, 50.5, 50.1, 49.8 (dien, 4 CH_2); signal of the free diol in the same solution: δ = 64.3 ppm. MS (FAB^+): *m*/*z* (%) = 293 (19) $[M + H]^+$, 292 (17) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1823 (vs, N–O), 1578 (w), 1453 (w), 1427 (w), 1073 (m), 1054 (m), 1033 (m), 749 (sh), 736 (st), 710 (st), 614 (m) cm^{-1}.

***mer*-Diethylenetriamine-{methyl-β-D-ribofuranosid-2,3-ato(2–)}-nitrosyl Ruthenium(III) Tetraphenylborate 5.5-Hydrate (4):** $Ru(NO)Cl_3 \cdot H_2O$ (0.256 g, 1.00 mmol) was suspended in water (10 mL) and diethylenediamine (0.103 g, 1.00 mmol) in water (2 mL) was added. A red solution formed immediately. Methyl-β-D-ribofuranoside (0.164 g, 1.00 mmol) dissolved in water (3 mL) was added followed by the dropwise addition of NaOH (1.5 mL, 2 M, pH ≈ 11.5). The reddish-brown solution was heated to 100 °C for 3 h (about half of the free glycoside was left in the reaction mixtures containing a 1:1 molar ratio of the ruthenium starting material and the furanoside; however, in terms of NMR spectra, no more product forms after prolonged reaction times). After cooling, sodium tetraphenylborate (0.342 g, 1.00 mmol) in water (15 mL) was added and a brown slurry precipitated. Over the course of 3 d, red crystals of **4** formed which were separated from the slurry by flotation (16% yield). Compound **4** is insoluble in water, ether and dichloromethane but dissolves in DMSO to yield a light-red solution. ^{13}C NMR (100 MHz, [D_6]DMSO): major isomer: δ = 111.3 (C1), 91.4 (C2), 89.7 (C3), 88.9 (C4), 65.1 (C5), 54.6 (C6); minor isomer: 112.3 (C1), 92.9 (C2), 88.8 (C3), 88.3 (C4), 64.0 (C5), 54.9 (C6); the signals of the phenyl residues of the counterion coincide for both isomers, the dien signals coincide partly: 164.7–163.2 (4 signals, phenyl, C_{ipso}), 136.1 (phenyl, C_{ortho}), 125.9 (phenyl, C_{meta}), 122.1 (phenyl, C_{para}); 50.9, 50.7, 50.5, 50.2, 49.9, 49.7 (dien, 4 CH_2 of 2 isomers) ppm.

Reaction of Cytidine with [*mer*-(dien)(NO)$RuCl_2$]PF_6: [*mer*-(dien)(NO)$RuCl_2$]PF_6 (52 mg, 0.116 mmol) was dissolved in sodium hydroxide (2 mL, 0.1 M, pH = 12.5). After addition of cytidine (56 mg, 0.232 mmol) the solution was heated in a microwave oven (10 min, 100 °C, 200 W with cooling). ^{13}C NMR spectroscopy indicated that about half of the nucleoside was bonded to ruthenium. Of this half, a major and a minor isomer are present in a ratio of about 2:1.

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