Mononuclear Rhodium(III) Complexes with N,N',N''-Trimethyl-1,1,1-tris(aminomethyl)ethane (Me₃-tame). Preparations, Characterization and Configurational Isomerization. Crystal Structure of meso-[Rh(Me₃-tame)₂](ReO₄)₃ · 1.2H₂O

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The reaction of $RhCl_3 \cdot aq$ with N,N',N''-trimethyl-1,1,1-tris(aminomethyl)ethane (Me₃-tame) in aqueous solution results in the formation of two isomers of [Rh(Me₃-tame)Cl₃] with C_3 and C_1 symmetry, respectively. The corresponding isomeric triaqua complexes were prepared from these trichloro complexes by mercury(II)/silver(I)-assisted aquation. Isomerization between the two isomers takes place in basic solution, and an equilibrated isomer mixture can be quenched by acidification. ^{13}C NMR was used to distinguish between the isomers.

The compound meso-[Rh(Me₃-tame)₂](CF₃SO₃)₃ was synthesized from [Rh(Me₃-tame)(H₂O)₃](CF₃SO₃)₃ (the isomer with C_3 symmetry), and by metathesis crystals of meso-[Rh(Me₃-tame)₂](ReO₄)₃ · 1.2H₂O, suitable for single-crystal X-ray diffraction, were obtained. This compound crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 10.184(2)$, $b = 17.559(4)$, $c = 9.161(4)$ Å and $\alpha = 90.68(3)$, $\beta = 112.57(3)$, $\gamma = 87.78(2)°$ and $Z = 2$. The geometries around the nitrogen atoms deviate considerably from ideal tetrahedral symmetry, and the rhodium–nitrogen bond lengths are relatively long [2.104(4)–2.120(5) Å]. In accordance with this, the biscomplex exhibits an unusually low ligand field strength, as determined from the electronic absorption spectrum.

Complexes of the facially coordinating ligand N,N',N''-trimethyl-1,1,1-tris(aminomethyl)ethane, Me₃-tame, have recently been investigated.[1–3] These works deal with the formation of trihydroxo-bridged homo- and hetero-dinuclear complexes of chromium(III) and cobalt(III). The magnetic and ESR properties,[1] crystal structures[1,2] and the equilibria between the dinuclear and mononuclear complexes[3] were examined. Compared to the large number of papers published on other tridentate facially coordinating amines, particularly the macrocyclic ligands 1,4,7-triazacyclononane (tacn) and 1,4,7-trimethyl-1,4,7-triazacyclononane,[4] the number of publications on Me₃-tame complexes has so far been small.[5–7]

An interesting feature of coordinated Me₃-tame is its ability to form configurational isomers, and coordination of Me₃-tame to rhodium(III) offers a unique possibility to study such isomerism due to the inertness of rhodium(III) complexes. In the present paper we report the preparation, characterization and isomerization of two isomers of [Rh(Me₃-tame)Cl₃] and of the two corresponding isomers of [Rh(Me₃-tame)(H₂O)₃]³⁺. An isomer of meso-[Rh(Me₃-tame)₂]³⁺ was also isolated and the crystal structure of meso-[Rh(Me₃-tame)₂](ReO₄)₃ · 1.2H₂O was determined.

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Results and discussion

Isomerism. Facial coordination of Me$_3$-tame to Rh^{III}L$_3$ (L being, e.g. Cl or H$_2$O) theoretically gives rise to eight isomers [see Fig. 1 (and Figs. 2 and 7)] in form of four pairs (**1-4**) of enantiomers. In Fig. 1, δ and λ refer to the conformation of the N–CH$_2$ bonds relative to the C_3 axis or the correspondingly situated pseudo three-fold axis, in the following called the C_1 axis. Because of the rigidity of the coordinated Me$_3$-tame, all three N–CH$_2$ bonds are expected to have the same conformation with respect to these axes. R and S refer to the configuration around the nitrogen atoms where, according to IUPAC rules, the hydrogen atom has been given the lowest priority (in Ref. 2 the dative bond was given the lowest priority resulting in the opposite R,S assignment).

Figure 1 illustrates that, of the four enantiomeric pairs, two pairs have C_3 symmetry (**1** and **4**), and two pairs have C_1 symmetry (**2** and **3**). In complex **1** the three N–CH$_3$ bonds are oblique relative to the C_3 axis (the CH$_3$–NH–CH$_2$–C torsion angle is close to 180°), and the three N–CH$_3$ methyl groups have a significantly longer distance to a methylene group than in complex **4**, where these bonds are nearly perpendicular to the C_3 axis (the CH$_3$–NH–CH$_2$–C torsion angle is close to 90°), assuming normal bond lengths and angles. In complex **2**, one of these three distances are short and in complex **3**, two are short. If this is decisive for the stability of the complexes, then this stability decreases from complex **1** to complex **4**.

A twist of the coordinated Me$_3$-tame ligand around the C_3 axis or the corresponding C_1 axis transforms a δ form into a non-enantiomeric λ form (or *vice versa*) as illustrated by the oblique arrows in Fig. 1.
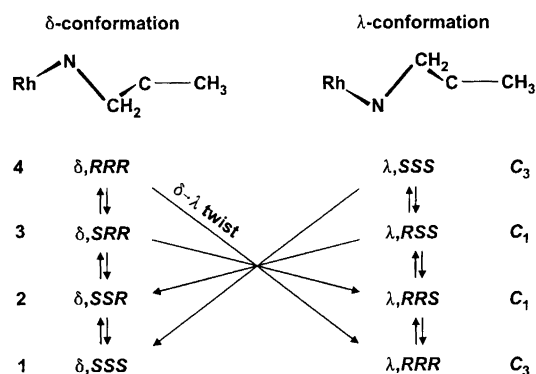
In the present work two isomers of [Rh(Me$_3$-tame)Cl$_3$]

Fig. 1. Illustration of the δ and λ conformation in a Rh(Me$_3$-tame) complex. Only one of the three Rh–N(CH$_3$)H–CH$_2$–C branches is shown. The three-fold (or pseudo-three-fold) axis goes through the rhodium atom and the methyl carbon atom. Below are shown the four enantiomeric pairs (**1-4**, with C_3 or C_1 symmetry) arising from the RS combinations of the configuration around the nitrogen atom. The vertical arrows indicate a stepwise base–catalyzed shift of this configuration, and the oblique arrows indicate a twist, simultaneous for the three branches, around the three-fold (or pseudo-three-fold) axis (cf. the Isomerism section).

have been isolated in the crystalline state, one with C_3 symmetry and one with C_1 symmetry (cf. Syntheses and NMR spectra). By aquation, the corresponding triaqua complexes were obtained, and the C_3 isomer could be isolated as the CF$_3$SO$_3^-$ salt. In hot basic solution (0.6 M OH$^-$ at 80 °C for 1–2 h, cf. Experimental) isomerization between the C_3 and C_1 forms takes place leading to an equilibrium mixture of the two forms with a ratio $K(C_3/C_1) = 5$ (cf. Experimental). The fact that this isomerization is most pronounced in basic solution indicates a mechanism involving deprotonation at a nitrogen atom. The abovementioned stability considerations suggest that the C_3 and C_1 isomers observed are complexes **1** and **2**. In all other Me$_3$-tame complexes with three-fold symmetry[1,2,7] only type **1** has been observed. If the energy barrier for a twist of the coordinated Me$_3$-tame around the C_3 or C_1 axis is low compared to the energy differences among the complexes **1-4**, then only complexes **1** and **2** are expected to be present in the base-catalyzed isomerization (cf. Fig. 1).

In the biscomplex, [Rh(Me$_3$-tame)$_2$]$^{3+}$, prepared by treating the C_3 isomer of [Rh(Me$_3$-tame)(H$_2$O)$_3$]$^{3+}$ with Me$_3$-tame. both ligands adopt the configuration of complex **1**, although this leads to more interligand crowdedness than with the complex **4** configuration (cf. Figs. 7 and 8 and the discussion of bond lengths and angles in the biscomplex). While there are several examples[6,8] of biscomplexes with analogous R–C(CH$_2$–NH$_2$)$_3$ ligands, there seems to be only one other well described biscomplex with Me$_3$-tame, namely the zinc(II) complex[7] (see Crystal structure).

Syntheses. Two of the four possible geometric isomers of [Rh(Me$_3$-tame)Cl$_3$] have been prepared and isolated. The isomer with C_1 symmetry is only slightly soluble in water, whereas the isomer with C_3 symmetry is more soluble. Both isomers lose part of the coordinated chloride in aqueous solution, even in 4 M HCl.

Complete replacement of chloride with water and removal of chloride was achieved by treatment with Ag$^+$ in the presence of Hg^{2+} in 3.5 M CF$_3$SO$_3$H. However, only the triaqua complex of the C_3 isomer could be isolated in the crystalline state. Treatment with Hg^{2+} alone also resulted in complete aquation. This was used for the preparation of samples of the pure triaqua complexes for ^{13}C NMR measurements (Fig. 2). Neither treatment with silver ions alone nor heating in neat CF$_3$SO$_3$H could remove all three coordinated chloride ions. Aquation of the trichloro complexes in 3.5 M CF$_3$SO$_3$H takes place with retention of configuration (see the next section on NMR spectra). Isomerization was achieved by reaction in hot basic solution. Subsequent cooling and addition of acid quenched the isomer equilibrium obtained. This method was used preparatively to obtain larger amounts of the trichloro complex with C_1 symmetry.

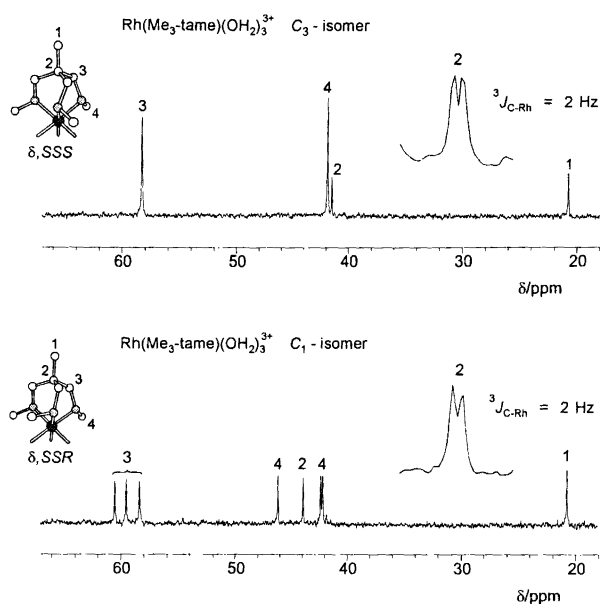The preparation of the bis(Me$_3$-tame) complex of rhodium(III) from the triaqua complex (C_3 symmetry)

Fig. 2. Proton decoupled ¹³C NMR spectra of C_3 and C_1 isomers of [Rh(Me₃-tame)(H₂O)₃]³⁺ (c_{Rh}=0.2 M in 3.5 M CF₃SO₃H). The inserts are the signals from the quaternary carbon atoms showing coupling to rhodium(III). The numbers at the signals refer to the numbers, shown on the structures, of the different carbon atoms identified by ¹³C DEPT spectra.

required repeated, prolonged treatment with excess Me₃-tame at elevated temperature.

NMR spectra. The ¹³C NMR spectra of the two isomeric triaqua complexes are shown in Fig. 2. The spectrum of one isomer shows four different signals in the intensity ratio approximately 3:3:1:1 which can be assigned to the three N–CH₂ groups, the three N–CH₃ groups, the quaternary carbon and the C–CH₃ methyl group in an arrangement with C_3 symmetry, whereas the spectrum of the other isomer shows eight equally intense signals in accordance with C_1 symmetry. The position of the signal from the C–CH₃ methyl group is the same for both isomers, whereas the position of the signal from the quaternary carbon atom differs. The relative concentrations of the two isomers in the isomerized solutions were determined by integration of the signals from the quaternary carbon atoms. The integral of the signal from this carbon atom of the C_3 isomer was found to be 1.2 times larger than the corresponding signal of the C_1 isomer by comparisons with standard solutions of the pure isomers and with a 1:1 mixture of the standard solutions.

Retention of configuration is demonstrated by the similarity of the ¹³C NMR spectra of the three-fold symmetrical trichloro, triaqua and biscomplex (the trichloro complex was the precursor for the triaqua complex, which again was the precursor for the biscomplex).

The signal from the quaternary carbon atoms shows coupling to rhodium with $^3J_{Rh-C}$ values of ca. 2 Hz in agreement with literature values.[9,10]
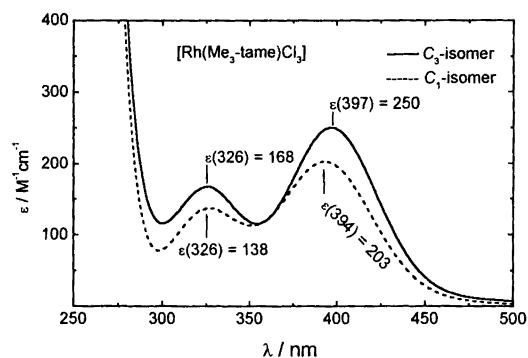

Fig. 3. Absorption spectra of the two isomers of [Rh(Me₃-tame)Cl₃] in 6 M HCl.
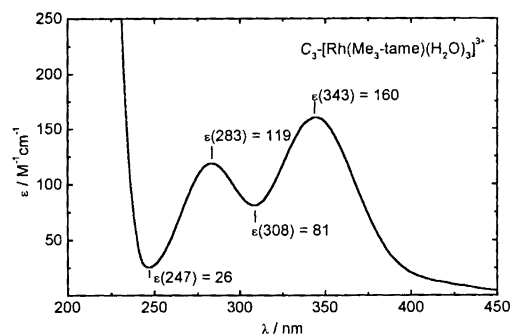
Fig. 4. Absorption spectrum of [Rh(Me₃-tame)(H₂O)₃]-(CF₃SO₃)₃ (C_3 isomer) in 1 M CF₃SO₃H. Rather similar spectra are found for the two triaqua isomers obtained from the corresponding trichloro complexes by treatment with silver(I) and mercury(II) in 3.5 M CF₃SO₃H at 80 °C for 3 h, followed by filtration and dilution to c_{Rh}=6 mM in 1 M CF₃SO₃H (maxima at 344 and 283 nm for both isomers).
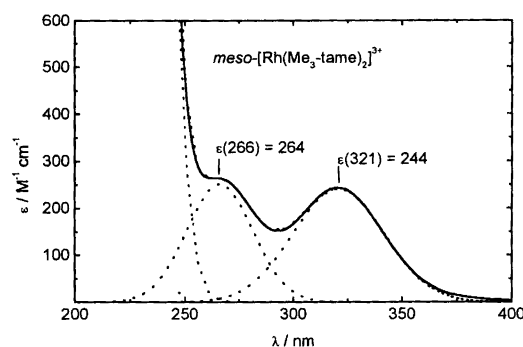
Fig. 5. Absorption spectrum of meso-[Rh(Me₃-tame)₂]-(CF₃SO₃)₃·H₂O in water and its Gaussian decompositions.

Spectral properties. The absorption spectra of the C_3 and C_1 isomers of [Rh(Me₃-tame)Cl₃] and [Rh(Me₃-tame)(H₂O)₃]³⁺ (C_3 isomer) and of meso-[Rh(Me₃-tame)₂]³⁺ are shown in Figs. 3–5. The spectrum of the C_3 isomer of [Rh(Me₃-tame)(H₂O)₃]³⁺ shows two transitions, at 343 and 283 nm, which are assigned to the two singlet transitions corresponding to $^1A_1 \rightarrow {}^1A_2, {}^1E$ and $^1A_1 \rightarrow {}^1A_1, {}^1E$, respectively. The lack of splitting is explainable by the holohedric symmetry being approximately O_h. As discussed in an earlier publication,[11] it is expected

that the energy of the first d–d band of the triaqua complex (343 nm; 2.92 μm^{-1}) is the average value of the energies of the first d–d bands in $[Rh(Me_3\text{-tame})_2]^{3+}$ and in $[Rh(H_2O)_6]^{3+}$ (397 nm; 2.52 μm^{-1}).[12] Using the values for the triaqua complex and the hexaaqua complex the calculated value of the first band in the biscomplex is found to be 3.31 μm^{-1} (302 nm), which is similar to the positions found for $[Rh(NH_3)_6]^{3+}$ (305 nm),[12] $[Rh(en)_3]^{3+}$ (301 nm),[12] $lel_3\text{-}[Rh(chxn)_3]^{3+}$ (302 nm),[12] $ob_3\text{-}[Rh(chxn)_3]^{3+}$ (303 nm),[12] $[Rh(tacn)_2]^{3+}$ (295 nm)[12] and in $[Rh(tn)_3]^{3+}$ (307 nm)[13] (en = ethane-1,2-diamine, chxn = cyclohexane-1,2-diamine, tn = propane-1,3-diamine). However, as seen from the spectrum of meso-$[Rh(Me_3\text{-tame})_2]^{3+}$, the position of $^1A_{1g} \rightarrow {}^1T_{1g}$ is 3.12 μm^{-1} (321 nm), which is significantly different from the expected value. Calculation[12] of the spectrochemical parameter Δ, $E(e_g) - E(t_{2g})$, and the Racah interelectronic repulsion parameter B from Gaussian resolution of the spectrum, gave the values $\Delta = 3.253 \ \mu m^{-1}$ and $B = 0.0434 \ \mu m^{-1}$ ($C = 4B$), which is the lowest d orbital splitting observed so far for homoleptical Werner type am(m)ine complexes ($\Delta = 3.395$; 3.420; 3.529 μm^{-1}, respectively, for $[Rh(tn)_3]^{3+}$, $[Rh(NH_3)_6]^{3+}$ and $[Rh(tacn)_2]^{3-}$).[12,13] The reason for this spectrochemical deviation is probably a result of interligand steric crowding of the two bulky ligands causing elongation of the rhodium–nitrogen bonds and distortion of the bond angles around the nitrogen atoms, as seen in the crystal structure of meso-$[Rh(Me_3\text{-tame})_2](ReO_4)_3 \cdot 1.2H_2O$.

Crystal structure of meso-*[Rh(Me₃-tame)₂](ReO₄)₃·1.2H₂O.* The triclinic structure consists of two rhodium(III) complexes, located at the inversion centres at the origin and the cell centre, respectively. Two molecules of Me₃-tame, thus related by inversion symmetry, coordinate to the rhodium ions in an octahedral *meso* form with nearly S_6 symmetry. It is noteworthy that even though the unit cell has room for exactly one fully occupied independent Rh complex, it is thermodynamically more favorable to keep inversion symmetry in the complex by having two half complexes. Three independent, ordered perrhenate ions, spaced ca. 4.1 Å between neighbouring rhenium atoms, and two water molecules (one of which has only 20% site population), occupy space between two $[Rh(Me_3\text{-tame})_2]^{3+}$ complexes. All perrhenate anions conform well with ideal tetrahedral symmetry with Re–O distances in the range 1.706(4)–1.736(4) Å and O–Re–O angles in the range 107.1(2)–110.6(2)°, and will not be discussed further. The three-dimensional structure is supported by an extensive hydrogen bonded network. The water molecule at the fully occupied site has hydrogen bonds to two of the perrhenate oxygen atoms (Table 1) the strength of which can be classified as medium. There is the possibility of at least one hydrogen bond from each of the six nitrogen atoms to oxygen atoms at water or perrhenate (Table 1). The distances suggest these bonds to be moderately weak. The crystal packing is illustrated in Fig. 6.

One $[Rh(Me_3\text{-tame})_2]^{3+}$ complex (Rh1) is disordered, in that the nitrogen atoms and the carbon atoms in the N–CH₃ groups are distributed over two sites with an 80.7(7)%/19.3(7)% probability distribution. The disorder reveals that 19% of the Rh1 complexes are rotated ca. 180° around a horizontal axis through Rh (cf. Fig. 8) relative to the 81%. Apart from the disorder of the Rh1 complex, there are no pronounced structural differences between the complexes. Comparison of chemically equivalent bond distances between the Rh1 complex with 81% population, and the Rh2 complex shows them to be identical within two estimated standard deviations. The Rh1 complex with 19% population has too large standard deviations for a comparison to be meaningful. The disorder might be correlated to that of the water molecule with 20% occupancy, even though no hydrogen bonds are observed to the 19% populated complex. The ordered Rh2 complex is shown in Fig. 7 with labelling of the atoms, and the double population of the Rh1 complex is illustrated in Fig. 8.

Both rhodium complexes in this crystal structure adopt the configuration of type 1, as discussed earlier (Isomerism). Table 1 gives selected bond distances and angles for the ordered complex. Most values agree well with those found in Me₃-tame complexes of chromium(III) (also of type 1).[1,2] However, a considerable deviation from ideal tetrahedral geometry around the nitrogen atoms is observed in the present study, Rh–N–C(T) = 119.8(3)–121.5(3)°, Rh–N–C(B) = 114.8(3)–116.0(3)° and C(B)–N–C(T) = 106.0(4)–107.8(4)°. For the chromium Me₃-tame complexes[1,2] the Cr–N–C(T) angles are at most 116.5(1)°, the Cr–N–C(B) angles in the same range as for Rh–N–C(B) and the C(B)–N–C(T) angles differ at most 1° from ideal tetrahedral. Only for one other bis(Me₃-tame) complex has the crystal structure been published,[7] namely for the $[Zn(Me_3\text{-tame})_2]^{2+}$ ion. This cation has a structure similar to that of the rhodium complex. It is located on a three-fold axis at an inversion centre and is therefore inherently also a *meso* form. The angles at nitrogen are Zn–N–C(T) = 119.0(6)°, Zn–N–C(B) = 114.1(6)° and C(B)–N–C(T) = 107.9(6)°, which is in agreement with our observations for $[Rh(Me_3\text{-tame})_2]^{3+}$. We may therefore conclude that in particular the deviations of the Rh–N–C(T) angles from ideal tetrahedral (increasing the C(T)–N^a distances) is most likely to originate from the interligand steric crowdedness of the two bulky ligands coordinated to one rhodium atom. This feature is also reflected in the bond distances. The Rh–N distances in the ordered complex range from 2.101(4) to 2.115(5) Å. A survey in the Cambridge Structural Database of well determined structures of rhodium(III) complexes with six nitrogen donor atoms from aliphatic amines yields, from 9 different complexes, distances in the range from 2.032 to 2.123 Å. Only two other complexes, one with the ligand 1-methyl-9-nitro-3,7,11,15,18,22-hexaazabicyclo(7.7.7)tricosane[14] and another with bis(3-aminopropyl)amine,[15] have distances in the same range. These two ligands are bulky

Table 1. Selected bond lengths (in Å) and bond angles (in °) for the ordered complex ion of *meso*-[Rh(Me3-tame)2](ReO4)3 · 1.2H2O.

Bond	Distance			Angle between atoms	Angle		
Rh2–N21	2.101(4)			N21–Rh2–N22	86.12(17)		
Rh2–N22	2.109(4)			N21–Rh2–N22[a]	93.88(17)		
Rh2–N23	2.115(4)			N21–Rh2–N23	86.69(16)		
				N21–Rh2–N23[a]	93.32(16)		
				N22–Rh2–N23	86.18(17)		
				N22–Rh2–N23[a]	93.82(17)		
	$j=1$	$j=2$	$j=3$		$j=1$	$j=2$	$j=3$
N2j–C2jB	1.500(6)	1.502(7)	1.501(7)	Rh2–N2j–C2jB	115.8(3)	115.2(3)	115.2(3)
N2j–C2jT	1.479(7)	1.484(6)	1.485(6)	Rh2–N2j–C2jT	119.9(3)	120.0(3)	121.6(3)
C2C–C2jB	1.529(7)	1.516(7)	1.518(7)	C2jB–N2j–C2jT	107.2(4)	107.3(4)	107.4(3)
C2C–C2F	1.525(7)			N2j–C2jB–C2C	112.8(4)	113.7(4)	113.2(4)
				C21B–C2C–C2jB		110.6(4)	111.1(4)
				C22B–C2C–C2jB			109.8(4)
				C2F–C2C–C2jB	107.8(4)	109.4(5)	108.1(4)

Numerical torsion angle	$j=1$	$j=2$	$j=3$
Rh2–N2j–C2jB–C2C	33.8(5)	32.5(5)	33.5(5)
N2j–C2jB–C2C–C2F	160.3(4)	160.5(4)	158.6(5)
C2jT–N2j–C2jB–C2C	170.6(4)	169.1(4)	172.5(4)

Hydrogen bonds	Distance	Hydrogen bonds	Distance
N21···O1W[c]	2.870(6)	N11···O33[c]	2.927(6)
N22···O23[e]	2.974(7)	N12···O32[d]	3.010(8)
N23···O14[f]	2.971(7)	N13···O1W[c]	2.882(7)
O1W···O34[b]	2.793(6)	N11'···O33[c]	2.86(2)
O1W···O12	2.884(6)	N12'···O32[d]	2.99(2)
O2W···O13[d]	2.73(2)	N13'···O1W[c]	2.91(2)
O2W···O23[d]	3.066(19)		

Symmetry operations: [a]($-x, -y, -z$). [b]($-x, 1-y, 1-z$). [c]($1-x, 1-y, 1-z$). [d]($1-x, 1-y, 2-z$). [e]($x, y, 1-z$). [f]($1-x, -y, 1-z$).
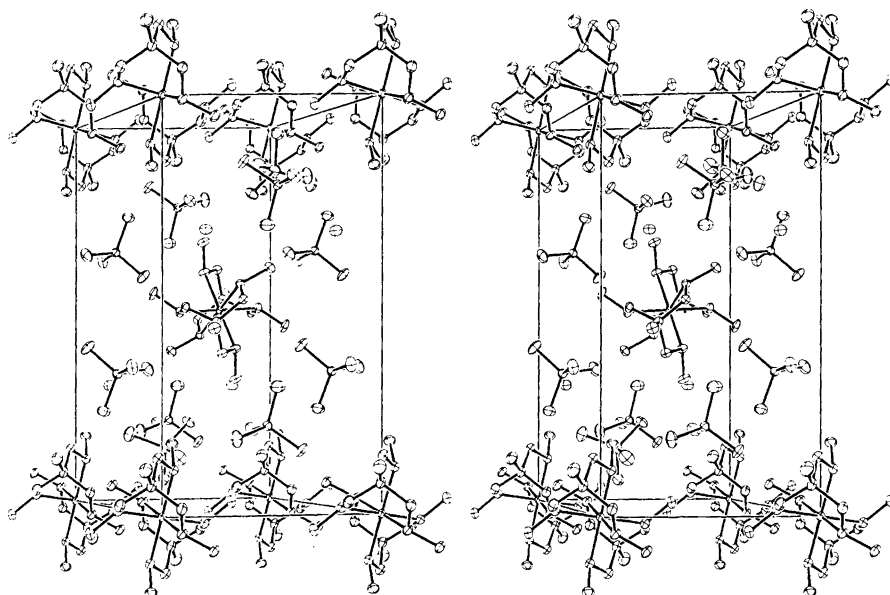
Fig. 6. Stereoscopic ORTEP[26] drawing of the unit cell of *meso*-[Rh(Me3-tame)2](ReO4)3 · 1.2H2O.

and can be considered to be sterically strained. Complexes with butane-2,3-diamine[16] and ethane-1,2-diamine[17–19] have Rh–N distances of 2.056 and 2.041–2.078 Å, respectively.

The torsion angles N–C(B)–C(C)–C(F), which range from 158.6(5) to 160.5(4)°, are in good agreement with the studies of the chromium complexes.[1,2] The C(T)–N–C(B)–C(C) torsion angles are approx. 170° in
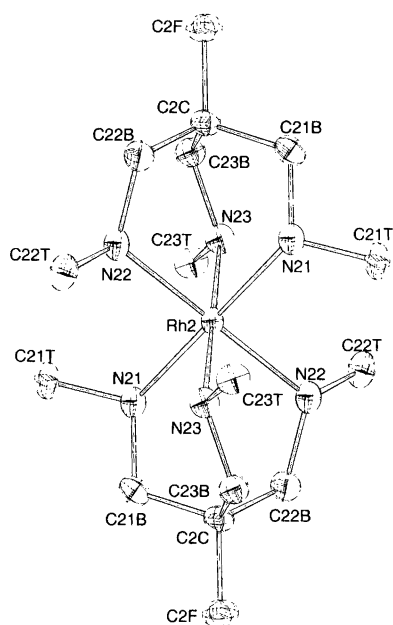
Fig. 7. ORTEP[26] drawing of the ordered *meso*-[Rh(Me₃-tame)₂]³⁺ ion with ellipsoids at the 50% probability level.

Fig. 8. ORTEP[26] drawing of the disordered *meso*-[Rh(Me₃-tame)₂]³⁺ ion showing the 19% populated atoms in blank, while fully and 81% populated atoms have filled ellipsoids, all at the 50% probability level.

the present complex of type **1**. A complex of type **4** would be expected to have this angle much closer to 90° (cf. the Isomerism section).

Experimental

Materials. N,N',N''-trimethyl-1,1,1-tris(aminomethyl)-ethane was prepared according to Kosowsky and Bailar.[5]

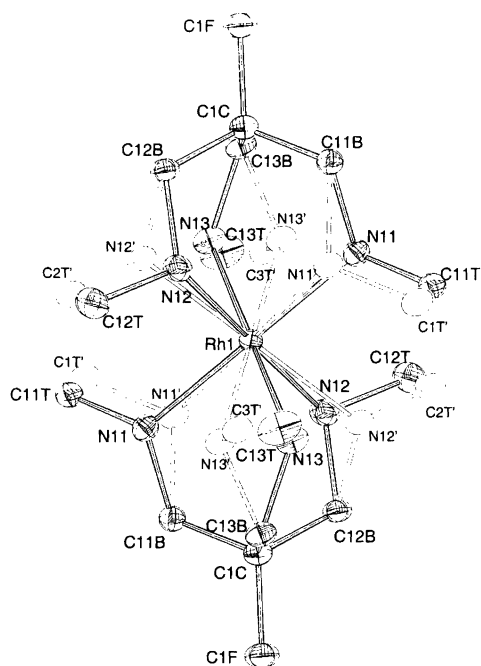Ag_2CO_3 was prepared in the following way: To a solution of 17.00 g of $AgNO_3$ (0.10 mol) in 20 ml of water was added a solution of 11.00 g of $KHCO_3$ (0.11 mol) in 50 ml of water dropwise with stirring as fast as the foaming allowed (ca. 20 min). After a further 10 min of stirring the yellow precipitate was filtered off, washed, first three times with water, then two times with ethanol, and finally two times with diethyl ether, and dried in air in the dark. Yield 13.6 g (99%). Two stock solutions were used: Solution A containing 1.00 M $AgCF_3SO_3$ in 3.5 M CF_3SO_3H was prepared by dissolution of 13.79 g of Ag_2CO_3 (50.0 mmol) in 100 ml of 4.5 M CF_3SO_3H followed by filtration, and solution B containing 0.50 M $Hg(CF_3SO_3)_2$ in 3.5 M CF_3SO_3H by dissolution of 10.83 g of HgO (50.0 mmol) in 100 ml of 4.5 M CF_3SO_3H. All other chemicals were obtained commercially in analytical or reagent grade and were used without further purification.

Instrumentation. Absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer. ¹³C NMR spectra were recorded on a Bruker AC 250 MHz Fourier-transform spectrometer. Single-crystal X-ray diffraction data were collected at 122 K on an Enraf-Nonius CAD-4 diffractometer.

Analyses. C, H, N and Cl analyses were carried out by the Micro-analytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

Synthetic procedures.

[Rh(Me₃-tame)Cl₃] (*C₃* and *C₁* isomer). In a 250 ml conical flask 1.00 g of $RhCl_3 \cdot 2H_2O$ (4.08 mmol) was dissolved in 60 ml of 0.1 M HCl, and 5 ml of ethanol were added followed by 0.72 g of Me₃-tame (4.5 mmol), which resulted in a red precipitate. By heating to 80 °C with stirring a clear, red solution was formed (less intensely coloured than before the addition of Me₃-tame). The solution was kept at 80 °C while a solution of 0.32 g of $LiOH \cdot H_2O$ (7.6 mmol) in 50 ml of water was added with stirring during a period of 15 min. After a further 15 min of heating 0.20 g of $LiOH \cdot H_2O$ (4.8 mmol) were added, and 15 min later the heating was stopped and the now yellow solution (pH ≈ 8.5) was filtered through a 0.45 μm pore size filter. 20 ml of 12 M HCl were added to the filtrate which was then evaporated to dryness on a rotatory evaporator (final temp. 80 °C). The residue was extracted for 2 h with 20 ml of ethanol and the mixture was filtered. The remanent was washed two times with ethanol and two times with diethyl ether and dried in air. Yield: 1.15 g (77%) of [Rh(Me₃-tame)Cl₃] (*C₃* and *C₁* isomer).

This product was extracted on the filter with 3 × 5 ml of 4 M HCl. The residue was washed with ethanol and diethyl ether and dried in air. Yield: 0.25 g (17%) of yellow [Rh(Me₃-tame)Cl₃] (*C₁* isomer). (Found: C 25.66; H 5.84; N 11.21; Cl 28.40. Calc. for $RhC_8H_{21}N_3Cl_3$: C 26.07; H 5.74; N 11.40; Cl 28.86).

The HCl extract was filtered through a 0.45 mm pore size filter and the filtrate was evaporated to dryness on a rotatory evaporator (final temp. 80 °C). The residue was then transferred to a filter with ethanol, washed with ethanol and diethyl ether, and dried in air. Yield: 0.75 g (50%) of yellow [Rh(Me$_3$-tame)Cl$_3$] (C_3 isomer). (Found: C 25.89; H 5.88; N 11.11; Cl 28.75. Calc. for RhC$_8$H$_{21}$N$_3$Cl$_3$: C 26.07; H 5.74; N 11.40; Cl 28.86). ^{13}C NMR (20% DCl) $\delta = 22.38$ (1C, s, H$_3$C–C), 39.70 (1C, s, –C–CH$_2$–), 42.90 (3C, s, –CH$_2$–N–) and 58.23 (3C, s, H$_3$C–N–).

[Rh(Me$_3$-tame)(H$_2$O)$_3$](CF$_3$SO$_3$)$_3$ (C$_3$ isomer). To 1.00 g of the C_3 isomer of [Rh(Me$_3$-tame)Cl$_3$] (2.70 mmol) were added (see Materials) 9 ml of solution A (9.0 mmol Ag$^+$) and 0.20 ml of solution B (0.10 mmol of Hg^{2+}) and the mixture was boiled until the yellow precipitate had dissolved and a white one had formed. The mixture was then heated at 80 °C for 3 h. The AgCl was filtered off and washed with two 2 ml portions of water. The filtrate and washings were evaporated as much as possible on a rotatory evaporator (final temp. 90 °C). After cooling in ice, 5 ml of diethyl ether were added, and the mixture was left overnight for crystallization. The yellow precipitate, which was contaminated with a black material, was filtered off, washed two times with diethyl ether, and dried in air. The residue was extracted on the filter with 2 × 1 ml of water, and the extract was filtered through a 0.45 μm pore size filter. To this filtrate were added two drops of 7.7 M CF$_3$SO$_3$H, and the solution was evaporated to nearly dryness over P$_4$O$_{10}$. The residue was transferred to a filter, washed three times with diethyl ether, and dried in air. Yield: 1.7 g (82%). (Found: C 17.15; H 3.47; N 5.42. Calc. for RhC$_{11}$H$_{27}$N$_3$S$_3$F$_9$O$_{12}$: C 17.31; H 3.57; N 5.50).

meso-[Rh(Me$_3$-tame)$_2$](CF$_3$SO$_3$)$_3$·H$_2$O. In a 100 ml beaker 1.20 g of the C_3 isomer of [Rh(Me$_3$-tame)(H$_2$O)$_3$](CF$_3$SO$_3$)$_3$ (1.57 mmol) were dissolved in 50 ml of water. 1 g of ethanol and 0.25 g of Me$_3$-tame (1.6 mmol) were added and the mixture was boiled for 10 min. After cooling to room temperature 0.25 g of Me$_3$-tame (1.6 mmol) and 1 g of ethanol were added and the mixture was heated in an oven at 60 °C for 24 h, 80 °C for 24 h, 100 °C for 24 h, and finally at 120 °C for 24 h. The resulting glass was extracted with two 10 ml portions of hot water. The extracts were filtered through a 0.45 μm pore size filter, and the filter was washed with water. The filtrate and washings were evaporated to dryness over P$_4$O$_{10}$. The residue was stirred with ethanol and the white precipitate was filtered off, washed, first twice with ethanol, then twice with diethyl ether, and dried in air. Yield: 0.50 g (36%). (Found: C 25.84; H 4.72; N 9.45; S 10.76. Calc. for RhC$_{19}$H$_{44}$N$_6$S$_3$F$_9$O$_{10}$: C 25.74; H 5.00; N 9.48; S 10.85). ^{13}C NMR (D$_2$O) $\delta = 22.24$ (1C, s, H$_3$C–C), 37.47 (1C, s, –C–CH$_2$–), 40.74 (3C, s, –CH$_2$–N–) and 58.64 (3C, s, H$_3$C–N–).

meso-[Rh(Me$_3$-tame)$_2$](ReO$_4$)$_3$·1.2H$_2$O. This salt was prepared in order to obtain crystals suitable for X-ray analysis: 0.45 g of *meso*-[Rh(Me$_3$-tame)$_2$](CF$_3$SO$_3$)$_3$·H$_2$O (0.51 mmol) were dissolved in 20 ml of water. 0.42 g of NH$_4$ReO$_4$ (1.6 mmol) were dissolved in 10 ml of water. The two solutions were filtered through 0.45 μm pore size filters, and the two filtrates were mixed by gentle swirling in order to obtain slow crystallization. The mixture was allowed to stand, first one day at room temperature, then 3 days at 8 °C after which the crystals were filtered off, washed, first two times with water, then two times with ethanol and finally two times with diethyl ether, and dried in air. Yield: 0.45 g (75%), (Found: C 16.27; H 3.56; N 7.04. Calc. for RhRe$_3$C$_{16}$H$_{44}$N$_6$O$_{13}$: C 16.15; H 3.73; N 7.06). If necessary, the compound can be recrystallized from boiling water (ca. 25 ml g^{-1}).

^{13}C NMR measurements. Proton decoupled ^{13}C NMR spectra were recorded at 62.896 MHz. Data, typically about 1 × 10^4 transients, were recorded at 300 K using a pulse width of 2 μs (45°), spectral width 14286 Hz, and 32 K data points giving a digitizer resolution of 0.872 Hz/point in the final spectrum. Under these conditions the acquisition time is 1.147 s per free induction decay. A relaxation delay of 1s between pulses was used. ^{13}C DEPT spectra[20] were used to achieve identification of the different kind of carbon atoms. Data were recorded with a delay time $\tau = 3.8$ ms and $\theta = 135°$. The solvent used for the NMR measurements of the triaqua complexes was non-deuterated and therefore a capillary with deuterium oxide was placed in the NMR tube for the deuterium lock. The symmetrical trichloro complex was measured in 20% DCl. Chemical shifts are reported on the δ scale with reference to internal 1,4-dioxane at $\delta = 67.4$ ppm.

Isomerization.

[Rh(Me$_3$-tame)Cl$_3$]. To 1.00 g of the C_1 isomer of [Rh(Me$_3$-tame)Cl$_3$] were added 20 ml of water. Then 0.50 g of LiOH·H$_2$O was added ([OH$^-$]=0.6 M) and the mixture was heated to 80 °C for 1 h. During the heating the precipitate dissolved and a yellow solution was formed. The solution was filtered through a 0.45 μm pore size filter. 25 ml of 12 M HCl were added to the filtrate which was then evaporated to dryness on a rotatory evaporator. The residue was extracted for 1 h with 20 ml of ethanol after which the precipitate was filtered off, washed twice with ethanol, then twice with diethyl ether, and dried in air. Yield: 92% of the mixture of the two [Rh(Me$_3$-tame)Cl$_3$] isomers, which were separated as described above by extraction with 3 × 5 ml of 4 M HCl, etc. giving 0.19 g (19%) of the C_1 isomer of [Rh(Me$_3$-tame)Cl$_3$] and 0.70 g (70%) of the C_3 isomer of [Rh(Me$_3$-tame)Cl$_3$].

The C_3 isomer of [Rh(Me$_3$-tame)Cl$_3$] reacted in exactly the same way (except that it dissolves already by the addition of water) yielding 94% of the mixture of the

two isomers, which after separation yields 14% of the C_1 isomer and 78% of the C_3 isomer.

$[Rh(Me_3\text{-}tame)(H_2O)_3]^{3+}$. To 60 mg of the C_1 isomer of $[Rh(Me_3\text{-tame})Cl_3]$ (0.162 mmol) were added (see Materials) 500 μl of solution A (0.50 mmol Ag^+) and 10 μl of solution B (0.005 mmol Hg^{2+}), and after shaking the mixture was kept at 80 °C for 3 h. Then the mixture was cooled, and the AgCl was filtered off (such solutions were used for the UV/VIS spectra, see Fig. 4) and washed with water. The filtrate, including the washings, were diluted with water to 100 ml and then concentrated on a column of Sephadex C-25 (3 cm × 1 cm⁰) followed by elution with 0.6 M NaOH. After heating for 2 h at 80 °C the eluate (1.0 ml) was cooled quickly, and 200 μl of 11 M CF_3SO_3H were added. ^{13}C NMR showed that this solution contained 17% of the C_1 isomer and 83% of the C_3 isomer of $[Rh(Me_3\text{-tame})(H_2O)_3]^{3+}$ (see NMR spectra).

The same procedure, starting with the C_3 isomer of $[Rh(Me_3\text{-tame})Cl_3]$, gave a solution containg 19% of of the C_1 isomer and 81% of the C_3 isomer of $[Rh(Me_3\text{-tame})(H_2O)_3]^{3+}$.

Crystal structure determination of meso-$[Rh(Me_3\text{-}tame)_2](ReO_4)_3 \cdot 1.2H_2O$. The title compound crystallizes as colourless transparent prismatic crystals. A crystal specimen bounded by faces ($\bar{1}\,\bar{1}\,0$), ($1\,1\,0$), ($0\,\bar{1}\,0$), ($0\,1\,0$), ($0\,\bar{1}\,1$), ($0\,1\,\bar{1}$), ($\bar{1}\,2\,1$) and ($1\,2\,\bar{1}$) was selected for data collection on a CAD-4 diffractometer with graphite monochromated Mo K_α radiation. The crystal was cooled to 122 K with an Oxford Cryo Systems nitrogen gas-flow system. The temperature was stable within 1 K during data collection. The unit cell parameters, $a = 10.184(2)$, $b = 17.559(4)$, $c = 9.161(4)$ Å and $\alpha = 90.68(3)$, $\beta = 112.57(3)$, $\gamma = 87.78(2)°$, were determined from a least-squares refinement of the setting angles of 20 reflections with θ in the range from 19.6 to 22.2°. The unit cell agrees with that determined by powder diffraction of the bulk material and the single crystal is thus representative of the bulk phase. The ω–2θ scan mode was used and the scan interval was set to $1.00° + 0.35°$ tan θ based on analysis of reflection profiles. Owing to the short b^* axis, scans of reflections which are high order in k have contributions from neighboring reflections. On integration it was therefore necessary to disregard the outer 10% of the scan in each side. Data

Table 2. Crystal and experimental data for meso-$[Rh(Me_3\text{-tame})_2](ReO_4)_3 \cdot 1.2H_2O$.

Crystal data:	
Formula	$Rh\{(CH_3NHCH_2)_3CCH_3\}_2(ReO_4)_3(H_2O)_{1.2}$
FW/g mol^{-1}	1193.69
Space group	Triclinic, $P\bar{1}$
Cell parameters, 122(1) K:	
a/Å	10.184(2)
b/Å	17.559(4)
c/Å	9.161(4)
$\alpha/°$	90.68(3)
$\beta/°$	112.57(3)
$\gamma/°$	87.78(2)
V/Å^3	1511.6(8)
Formula units per cell, Z	2
Calculated density (122 K)/g cm^{-3}	2.622
Data collection and SHELXL97 refinement:	
Radiation (Mo K_α) λ/Å	0.71073
Crystal size/mm^3	$0.28 \times 0.18 \times 0.10$
Linear absorption coefficient, μ/mm^{-1}	12.705
Minimum and maximum transmission	0.103, 0.394
θ limits/°	1–35
(hkl) limits	h: $-16 \rightarrow 15$, k: $-28 \rightarrow 28$, l: $0 \rightarrow 14$
No. of measurements	14953
No. of independent measurements	13295, 11189 with $I > 2\sigma(I)$
Internal R value	0.0277
No. of standard reflections, frequency	4, every 10000 s
Intensity decay	0–27%
No. of parameters	399
LSQ weights	$w^{-1} = \sigma^2(F_o^2) + 0.04P$, where $P = (F_o^2 + 2F_c^2)/3$
$R(F)$ [for $F^2 > 2\sigma(F^2)$]	0.0386
$wR(F^2)$ (all reflections)	0.0982
S_{all}	1.200
Max. shift in last cycle, $(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$/e Å^{-3}	2.509
$\Delta\rho_{min}$/e Å^{-3}	−3.823
Extinction coefficient	0.00263(15)

Table 3. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters (in Å^2) for *meso*-[Rh(Me₃-tame)₂](ReO₄)₃ · 1.2H₂O.

Atom	x	y	z	U_{eq}
Anions:				
Re1	0.43050(2)	0.151175(12)	0.73210(2)	0.02392(5)
O11	0.3400(5)	0.0676(3)	0.6963(6)	0.0349(9)
O12	0.3469(4)	0.2157(3)	0.5793(5)	0.0301(8)
O13	0.4409(5)	0.1879(3)	0.9117(6)	0.0401(11)
O14	0.6017(5)	0.1304(3)	0.7439(7)	0.0431(12)
Re2	0.005147(18)	0.214223(11)	0.52541(2)	0.01949(4)
O21	0.0420(4)	0.1560(3)	0.3908(5)	0.0289(8)
O22	0.0283(5)	0.3085(3)	0.4908(7)	0.0374(10)
O23	0.1148(4)	0.1877(3)	0.7161(5)	0.0357(10)
O24	−0.1681(4)	0.2041(3)	0.5086(6)	0.0304(8)
Re3	0.217850(18)	0.658843(10)	0.88885(2)	0.01822(4)
O31	0.2236(5)	0.7496(3)	0.8275(6)	0.0356(9)
O32	0.3392(4)	0.6470(3)	1.0817(5)	0.0339(9)
O33	0.2560(5)	0.5936(3)	0.7665(6)	0.0357(10)
O34	0.0512(4)	0.6425(3)	0.8868(5)	0.0307(8)
Cations:				
Rh1	0.5000	0.5000	0.5000	0.01250(7)
C1C	0.8344(4)	0.4656(3)	0.6742(5)	0.0168(6)
C1F	0.9947(5)	0.4480(3)	0.7596(6)	0.0240(8)
C11B	0.8112(4)	0.5199(2)	0.5384(5)	0.0165(6)
C12B	0.7625(4)	0.3908(3)	0.6126(5)	0.0178(7)
C13B	0.7795(4)	0.5021(3)	0.7937(5)	0.0184(7)
N11[a]	0.6689(5)	0.5617(3)	0.4839(5)	0.0166(8)
C11T[a]	0.6499(6)	0.6011(4)	0.3331(8)	0.0207(10)
N12[a]	0.6186(5)	0.4014(3)	0.4819(6)	0.0196(9)
C12T[a]	0.5531(6)	0.3261(4)	0.4479(9)	0.0240(11)
N13[a]	0.6211(5)	0.4942(3)	0.7467(6)	0.0192(9)
C13T[a]	0.5812(7)	0.5419(5)	0.8586(7)	0.0270(13)
N11′[b]	0.657(2)	0.5195(12)	0.409(2)	0.018(3)
C1T′[b]	0.627(3)	0.5814(17)	0.290(4)	0.021(5)
N12′[b]	0.6111(19)	0.3942(11)	0.585(2)	0.016(3)
C2T′[b]	0.554(3)	0.3216(15)	0.512(3)	0.019(4)
N13′[b]	0.640(2)	0.5497(12)	0.707(2)	0.019(3)
C3T′[b]	0.593(3)	0.5740(16)	0.838(3)	0.019(4)
Rh2	0.0000	0.0000	0.0000	0.01607(8)
C2C	0.2887(5)	0.0864(3)	0.1728(6)	0.0218(8)
C2F	0.4277(6)	0.1265(4)	0.2571(7)	0.0307(11)
N21	0.1035(4)	0.0219(2)	0.2427(5)	0.0215(7)
C21B	0.2569(5)	0.0415(3)	0.2967(6)	0.0247(8)
C21T	0.0921(6)	−0.0318(3)	0.3601(6)	0.0278(9)
N22	0.0430(5)	0.1133(2)	−0.0353(5)	0.0217(7)
C22B	0.1704(5)	0.1453(3)	0.0934(6)	0.0240(8)
C22T	−0.0726(6)	0.1731(3)	−0.0793(7)	0.0263(9)
N23	0.2038(4)	−0.0291(3)	0.0008(5)	0.0221(7)
C23B	0.3079(5)	0.0337(3)	0.0494(6)	0.0242(8)
C23T	0.2216(5)	−0.0694(3)	−0.1342(6)	0.0241(8)
Solvent water molecules:				
O1W	0.2254(4)	0.3088(2)	0.3046(5)	0.0241(7)
O2W[c]	0.7176(19)	0.6887(11)	1.057(2)	0.024(3)

Occupation factors: [a] 0.807(7). [b] 0.193(7). [c] 0.20. Remaining occupancies are 1. The occupation factors should be multiplied by the crystallographic site multiplicity to obtain the number of atoms in the unit cell. The equivalent, isotropic displacement parameter is defined as $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

were reduced using DREADD.[21,22] Integration, background subtraction, and correction for Lorentz and polarisation effects was performed. As the intensity control reflections differed considerably in decay during the

7 days of data collection, anisotropic scaling according to the nearest reciprocal axis was performed for all reflections. Absorption was corrected for using the Gaussian integration method (ABSORB).[23] Reflections

were sorted and averaged in Laue group $\bar{1}$. Crystal data and details about the structure determination are listed in Table 2 and atomic coordinates and thermal parameters are listed in Table 3.[24]

13 295 unique reflections were included into SHELXS-86[24] and used for a Patterson search. This gave the positions of the three rhenium atoms and one rhodium atom. Subsequent difference Fourier syntheses revealed the remaining non-hydrogen atoms. The structure was refined with SHELXL-97.[25] Hydrogen atoms were included in calculated positions assuming ideal geometry, and refined using a riding motion on the atoms to which they are bound. The 19% populated Rh1 complex was established after introduction of anisotropic thermal vibration parameters of all non-hydrogen atoms, where it was noted that $C_i(T)$ atoms had unusually large anisotropic parameters and that there were positive remanence peaks close to the nitrogen atoms. The final difference densities are high, from 2.52 to $-3.83 \, \mathrm{e\,\mathring{A}^{-3}}$. However, all positive peaks higher than $1.15 \, \mathrm{e\,\mathring{A}^{-3}}$ and all density holes deeper than $-0.90 \, \mathrm{e\,\mathring{A}^{-3}}$ are situated either close to rhenium or rhodium atoms or between rhenium and the oxygen atoms to which they are bonded. These differences can be ascribed to insufficiences in the absorption correction, the anisotropic decay of the crystal, and possibly also to poor description of the scattering factors for rhenium and rhodium atoms. The distribution of remanence peaks otherwise reveals no systematic pattern. Figures have been prepared using ORTEP-II.[26] Tables of anisotropic thermal parameters and a listing of observed and calculated structure factors are available from one of the authors (A.F.J.) on request.

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