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Oxidorhenium(V) complexes with tetradentate thiourea derivatives

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ABSTRACT

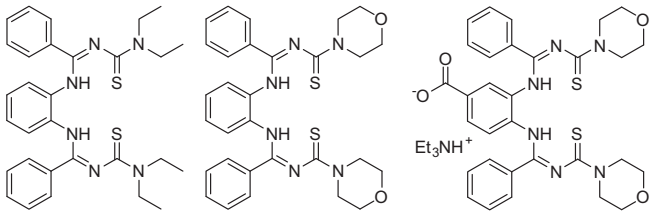
Potentially tetradentate, binegative thiocarbamoylbenzamidines derived from *o*-phenylenediamines (H_2L or H_3L) are shown to be suitable ligand systems for oxidorhenium(V) cores. They readily react with $(NBu_4)[ReOCl_4]$ or $[ReOCl_3(PPh_3)_2]$ under formation of monoxido complexes of the composition $[ReO\{(H)L\}(Y)]$ with various co-ligands (Y = ReO_4^-, $F_3CCO_2^-$, Cl^- or methanol) or μ-oxido dimers depending on the reaction conditions applied. Representative products were isolated and studied spectroscopically and by X-ray diffraction.

Substitutions in the periphery of the ligands allow the introduction of a carboxylic substituent, which may serve as anchor group for future bioconjugation of appropriate rhenium (or technetium) complexes.

1. Introduction

Tri-, tetra- or multiple-dentate ligands, which form stable or kinetically inert complexes with rhenium and technetium are of permanent interest for modern nuclear medical labeling procedures, since previous studies have shown that mono- and bidentate ligand systems may suffer from insufficient *in vivo* stability due to rapid ligand exchange reactions with plasma components [1–9]. For common technetium(V) and rhenium(V) cores, particularly ligands with 'medium' and 'soft' donor atoms are recommended [1,2]. Thus, chelators with a mixed sulfur and nitrogen donor sphere should be very suitable and some of them have been found application in routine nuclear medical procedures. One focus of current research in this field is the search for suitable chelating systems for bioconjugation procedures. Such ligands must (i) form thermodynamically stable and/or kinetically inert complexes with one or more of the common metal cores (e.g. $\{M=O\}^{3+}$, $\{MN\}^{2+}$, $\{M(CO)_3\}^+$; M = Tc, Re) and (ii) possess a suitable anchor group, which does not contribute to the coordination of the metal, but is able to form stable bioconjugates (e.g. carboxylates, aldehydes, alkynes).

Thiourea derivatives have been shown to be excellent bi- and tridentate ligands for Re(V) oxido-, nitrido-, and phenylimido cores [10–20]. Particularly thiocarbamoylbenzamidines are highly flexible ligands [13–19]. They are prepared from benzimidoyl chlorides and amines, which allows access to a large number of ligands with various donor sites. Tetradentate ligands are formed when two equivalents of the corresponding benzimidoyl chloride are coupled to diamines. H_2L^1 and H_2L^2 can act as



tetradentate, binegative ligands and form stable complexes with metal ions, which can adopt square-planar or pyramidal coordination spheres. Keeping in mind the structures of such ligands with metal ions like Ni^{2+} or Cu^{2+} [20,21], the tetradentate chelators should also be suitable for the coordination of the equatorial coordination spheres of oxidotechnetium(V) and oxidorhenium(V) complexes.

In the present paper, we report about the coordination chemistry of H_2L^1 and H_2L^2 with oxidorhenium(V) centers as models for further studies with technetium, as well as the synthesis and coordination chemistry of a novel *SNNS* proligand with an additional carboxylic group for future bioconjugation, $(Et_3NH)(H_2L^3)$.

2. Results and discussion

N,N-[(Dialkylamino)-*N*′-(thiocarbonyl)]benzamidines can readily be varied in their periphery. This has been demonstrated with

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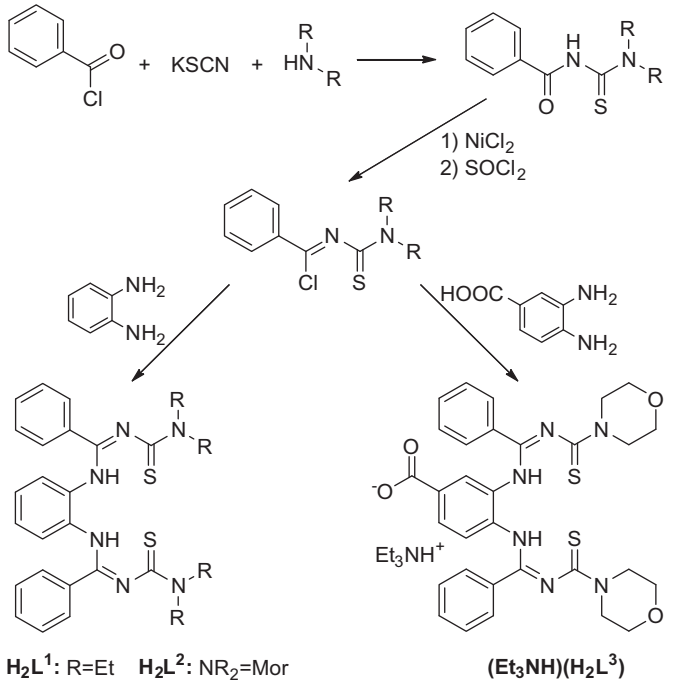
a number of bi- and tridentate examples before. Such modifications help to tune their properties or couple them to biomolecules. With regard to the molecular building blocks, which are used for the synthesis of the ligands, benzoyl chloride, ammonium thiocyanate, secondary amines and a second (functionalized) amine, there exist several positions, where functional groups for bioconjugation can be introduced. For the potentially tetradentate ligands under study, we have chosen the central phenylendiamine unit for substitution with an additional carboxylic group (Scheme 1). This has the advantage, that only one molecular position will contribute in future bioconjugation procedures, while substitution of the benzoyl or amine units would result in two possible coupling positions, which might cause problems in order to produce one unique coupling product.

The proligands H_2L^1 and H_2L^2 were prepared as almost colorless solids from the corresponding benzimidoyl chlorides and *o*-phenylenediamine. Previous attempts to prepare these compounds ended in the isolation of crude, oily products, which have directly been used for the syntheses of the corresponding Cu(II) and Ni(II) complexes [20,21]. Some slight modifications during the ligand synthesis, particularly the use of THF instead of acetone, improve the yields and allow the isolation of H_2L^1 and H_2L^2 in pure form. They were characterized by elemental analysis and spectroscopic methods. IR spectra of the compounds exhibit medium absorptions around 3250 cm^{-1} and very strong bands in the region between 1590 and 1640 cm^{-1}, which are assigned to ν_{NH} and $\nu_{C=N}$ stretches respectively. ^1H NMR spectra confirm the symmetric structure of the products. Thus, the resonances of the aromatic protons of the *o*-phenylenediamine residue appear as two doublets at around 6.40 and 6.80 ppm. Two series of signals corresponding to alkyl groups of the NR^1R^2 residues are also observed, but are less resolved, which reflects the hindered rotation of the thiourea moiety.

The carboxylate-substituted proligand $(H_2L^3)^-$ was prepared analogously to H_2L^2. After removal of a brownish solid, it can be isolated from the remaining solution as triethylammonium salt. The ^1H NMR spectrum of the products confirms the ionic nature of the compound, since the signals of the $(Et_3NH)^+$ can clearly be detected with a correct ratio besides those which can be assigned to the thiocarbamoylbenzamidine. Chemical shifts and ratio of the observed signals are similar to those of H_2L^2 and shall not be discussed here in detail. Further support for the composition of $(Et_3NH)(H_2L^3)$ is given by the ESI mass spectra of the compound. The ESI(−) spectrum is clearly dominated by the molecular ion of the $(H_2L^3)^-$ at m/z = 615.1888 (Calc. 615.1854), while the positive mode spectrum shows the $(Et_3NH)^+$ cation as base peak together with a less intense peak at m/z = 617.2014 (Calc. 617.2004), which can be assigned to the doubly protonated $(H_4L^3)^+$ ion.

Reactions of the potentially tetradentate proligands with the common precursor $[ReOCl_3(PPh_3)_2]$ gave insoluble red or brown solids, from which no crystalline products could be isolated. More controlled reactions are possible starting from $(NBu_4)[ReOCl_4]$. Thus, H_2L^1 reacts with $(NBu_4)[ReOCl_4]$ and Et_3N as supporting base in MeOH under formation of a red crystalline precipitate of the composition $[ReO(L^1)(OReO_3)]$. The yield is only about 20%, which can be explained by the rapid formation of perrhenate. Such side-reactions are not unusual in the chemistry of oxidorhenium(V) complexes and were previously found as results of hydrolysis followed by disproportion or oxidation of the anionic complex $[ReOCl_4]^-$ (to ReO_2 and ReO_4^- or ReO_4^- exclusively) [2,22–28]. The IR spectrum of $[ReO(L^1)(OReO_3)]$ shows no band in the region above 3100 cm^{-1}, which could be assigned to an NH stretch, and the intense $\nu_{C=N}$ absorption in the spectrum of H_2L^1 at 1640 cm^{-1} is shifted by about 100 cm^{-1} to longer wavelengths. This indicates the expected double deprotonation and chelate formation of the ligand. While the terminal {Re = O} core is confirmed by a medium absorption at 983 cm^{-1}, the presence of coordinated ReO_4^- is indicated by a very strong absorption at 921 cm^{-1} [2]. The ^1H NMR spectrum of the product reveals its symmetric structure, in which two benzamidine parts are magnetically equivalent and, thus, a planar coordination mode of $\{L^1\}^{2-}$ is suggested. As the consequence of hindered rotation around the C–N bonds in the $C(S)–NEt_2$ moieties and the inflexible structure, two well resolved triplets and four multiplets are observed for the ethyl protons. The FAB^+ MS spectrum of $[ReO(L^1)(OReO_3)]$ does not show the molecular ion peak, but exposes an intense fragment at m/z = 745 with the isotopic pattern of a mononuclear rhenium complex, which can be assigned to $[ReO(L^1)]^+$. Such a fragmentation pattern is not unusual and confirms the weakness of the bond to ReO_4^- and the ready dissociation of this ligand.



Scheme 1. Synthesis of the ligands used in this paper.

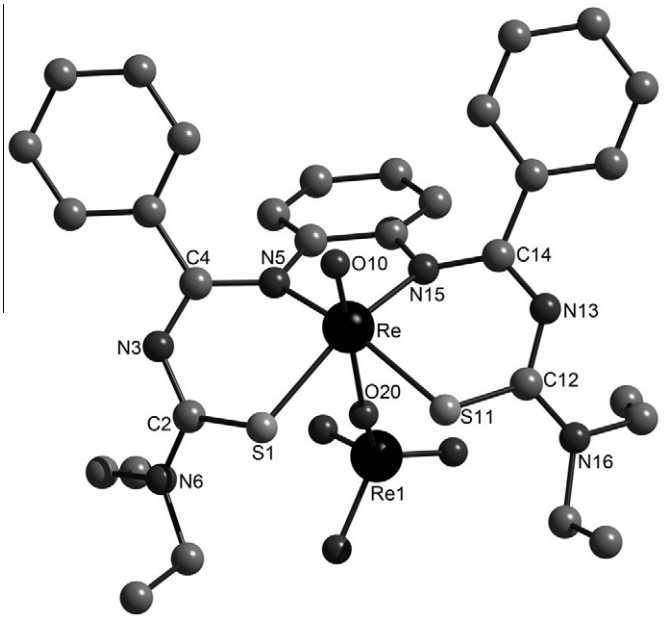


Fig. 1. Molecular structure of $[ReO(L^1)(OReO_3]$ [35]. H atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) in the molecular structures of $[ReO(L^1)(OReO_3]$, $[\{ReO(L^2)\}_2O]$, $[ReO(L^3)(MeOH)]$ and $[ReO(L^3)(TFA)]$.

	$[ReO(L^1)(OReO_3)]$	$[\{ReO(L^2)\}_2O]$	$[ReO(L^3)(MeOH)]$	$[ReO(HL^3)(TFA)]$
Re–O10	1.669(4)	1.711(7)	1.669(7)	1.665(5)
Re–O20	2.350(4)	1.919(1)	2.355(6)	2.272(5)
Re–S1	2.364(2)	2.379(3)	2.339(3)	2.360(2)
Re–N5	2.024(5)	2.062(8)	2.033(9)	2.036(5)
Re–S11	2.360(2)	2.382(3)	2.334(3)	2.342(2)
Re–N15	2.019(5)	2.112(7)	2.002(9)	2.019(6)
S1–C2	1.748(7)	1.75(1)	1.77(1)	1.740(7)
C2–N3	1.341(8)	1.32(2)	1.32(2)	1.356(8)
N3–C4	1.298(8)	1.31(1)	1.32(1)	1.304(8)
C4–N5	1.367(8)	1.37(1)	1.35(1)	1.345(8)
S11–C12	1.761(6)	1.73(1)	1.74(1)	1.753(8)
C12–N13	1.344(8)	1.32(1)	1.34(1)	1.343(9)
N13–C14	1.302(7)	1.32(1)	1.31(1)	1.307(8)
C14–N15	1.356(8)	1.34(1)	1.38(1)	1.365(8)
O10–Re–O20	178.5(2)	177.4(4)	178.0(3)	175.4(2)
O10–Re–S1	100.5(2)	94.5(3)	101.1(3)	99.3(2)
O10–Re–N5	100.9(2)	93.4(3)	100.8(4)	100.7(2)
O10–Re–N15	102.0(2)	91.7(3)	100.8(3)	100.1(2)
O10–Re–S11	101.5(1)	94.8(3)	102.0(3)	101.6(2)
S1–Re–O20	78.8(2)	87.7(3)	80.6(2)	78.6(1)
S1–Re–N5	93.6(2)	94.8(2)	92.9(2)	94.9(2)
S1–Re–N15	157.2(1)	171.9(2)	158.0(2)	160.5(2)
S1–Re–S11	84.45(6)	90.5(1)	85.7(1)	85.39(6)
N5–Re–O20	77.8(2)	85.3(2)	77.9(3)	75.6(2)
N5–Re–N15	79.5(2)	79.6(3)	80.1(3)	79.5(2)
N5–Re–S11	157.5(1)	169.8(2)	156.9(2)	157.4(2)
N15–Re–O20	78.6(2)	85.8(4)	77.5(3)	81.9(2)
N15–Re–S11	93.7(1)	94.2(2)	92.6(2)	92.7(2)
S11–Re–O20	79.8(2)	86.20(9)	79.1(2)	82.4(2)
Re–O20–X[a]	164.8(3)	174.7(6)	129.2(7)	132.1(5)

[a] X = Re2 for $[ReO(L^1)(OReO_3)]$, X = Re′ for $[\{ReO(L^2)\}_2O]$, X = C21 for $[ReO(L^3)(MeOH)]$ and $[ReO(HL^3)(TFA)]$.

The spectroscopic analysis of $[ReO(L^1)(OReO_3)]$ is confirmed by the results of an X-ray structure determination. Fig. 1 depicts the molecular structure of the complex and selected bond lengths and angles are presented in Table 1. The rhenium atom is coordinated in a distorted octahedral environment with a terminal oxido ligand and a perrhenato unit in axial positions. The $\{L^1\}^{2-}$ ligand is arranged in the equatorial plane and binds symmetrically to the rhenium atom as an $\{N_2S_2\}$ tetradentate ligand. The Re atom is placed 0.425(2) Å above this plane towards the oxido ligand. In this arrangement, all phenyl rings are bent out of the equatorial plane. While the Re1–O10 bond length of 1.669(4) Å falls within the common range of rhenium–oxygen double bonds, the Re1–O20 distance of 2.350(2) Å is much longer than a typical rhenium–oxygen single bond and reflects only weak interactions between the perrhenato ligand and the Re atom of the chelate. Consequently, the Re2–O20 distance is only a little longer than those of the other Re–O bonds in the perrhenato unit.

In order to prevent the undesired formation of $[ReO_4]^-$, which is frequently observed, when the removal of chlorido ligands from $[ReOCl_4]^-$ by the addition of a supporting base under atmospheric and hydrous conditions is faster than the stabilization of the $\{ReO\}^{3+}$ center by incoming ligands, the synthetic procedure was slightly modified. The supporting base was just added after heating the mixture of $(NBu_4)[ReOCl_4]$ and one equivalent of H_2L^2 in MeOH for a period of 5 min (reactions under consequently anhydrous and anaerobic conditions have not been undertaken with regard to the nuclear medical background of the present study). A red solid of the composition $[\{ReO(L^2)\}_2O]$ precipitated directly from the reaction mixture and was isolated in high yield. The compound was recrystallized from CH_2Cl_2/acetone and characterized spectroscopically and by X-ray diffraction. Fig. 2 shows a structural plot and selected bond lengths and angles are summarized in Table 1. A central oxido ligand links two $\{ReO(L^2)\}^+$ units. Thus, the rhenium atoms in the symmetry-related subunits have a distorted coordination environment. The Re1–O20–Re1′ angle is 175.5(7)°. Expectedly, the Re–O20 bond of 1.918(1) Å is clearly longer than the bond to the terminal oxido ligand (1.738(1) Å), but reflects some double bond character. The donor atoms of the tetradentate ligand are planar within 0.005 Å, and the rhenium atom is situated outside this plane by 0.141(4) Å towards O10.

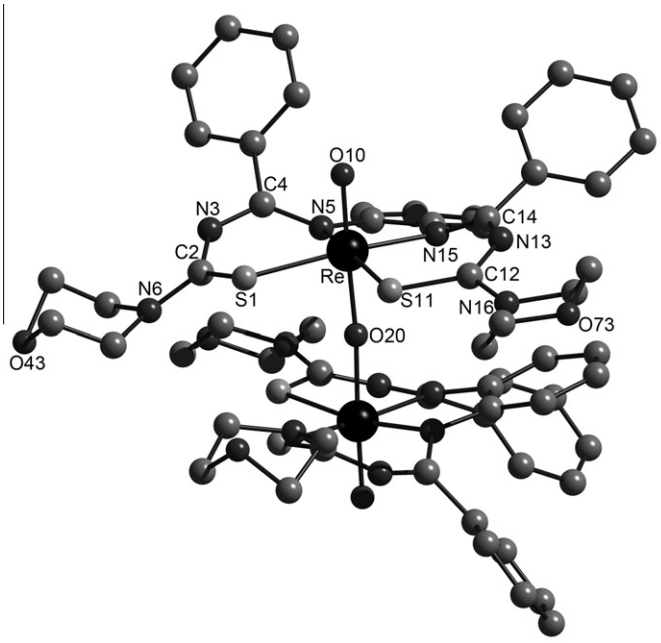


Fig. 2. Molecular structure of $[\{ReO(L^2)\}_2O]$ [35]. H atoms have been omitted for clarity.

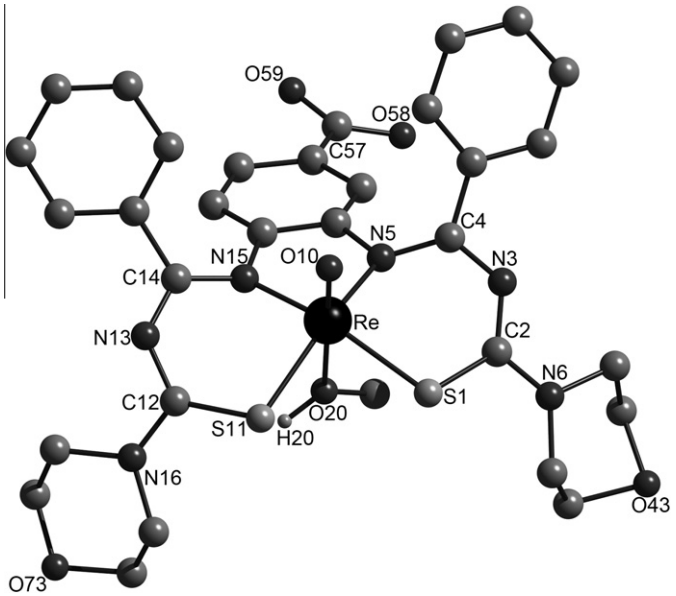


Fig. 3. Molecular structure of [ReO(L^3)(MeOH)] [35]. H atoms on carbon atoms have been omitted for clarity.

The ^{1}H NMR spectrum of [{ReO(L^2)}$_2$O] is complex. Expectedly, the CH_2 signals of the morpholine moieties appear as an overlapping array which is poorly resolved. But also the protons of the central phenylene diamine ring show four different signals. This indicates that the magnetic inequivalence of the phenyl rings in the solid state structure of the complex is also present in solution. Obviously, a hindered rotation around the Re–O20–Re′ bonds is responsible for this result. The FAB$^+$ MS spectrum does not show the molecular ion peak of the dimeric compound, but a peak of high intensity at m/z = 774.9, which can be assigned to the fragment cation [ReO(L^2)]$^+$. A less intense signal at m/z = 790.8 corresponds to a fragment of the composition [ReO(H_2O)(L^2)]$^+$.

The reaction of the carboxyl-substituted proligand (Et_3NH)[H_2L^3] with (NBu_4)[$ReOCl_4$] in a chloroform/methanol mixture proceeds at room temperature without the addition of any base. Single crystals of [ReO(L^3)(MeOH)] with co-crystallized $CHCl_3$ and water were obtained after a couple of days by slow evaporation of the reaction mixture. The X-ray structure analysis of these crystals confirm the formation of a six-coordinate rhenium complex with a general coordination environment as was observed before for [ReO(L^1)]($OReO_3$)] with the axial coordination position trans to the oxido ligand being occupied by a methanol ligand instead of perrhenate. A structural plot is given in Fig. 3, and selected bond lengths and angles are collected in Table 1. The coordination of a methanol ligand instead of a methanolato one is strongly suggested by the relatively long Re–O20 bond length of 2.355(6) Å and the Re–O20–C21 angle of 129.2(7) Å. In all hitherto structurally characterized complexes with trans-{O=Re–OMe}$^{2+}$ cores, the Re–O–Me angles are higher [29], which is the result of significant transfer of electron density from the terminal oxido ligand to the trans-situated Re–O bond and is also reflected by a shortening of this bond in comparison to Re–O single bonds in the equatorial coordination sphere of such complexes [16]. The carboxylic group in the periphery of the tetradentate ligand is deprotonated in the solid state structure under study. This can be deduced by almost equal C–O bond lengths of 1.259(16) and 1.262(16) Å, respectively. Additional support for the coordination of a neutral methanol ligand and the deprotonation of the carboxylic group is given by the formation of an extended network of hydrogen bonds, in which they are involved together with the co-crystallized water molecules. The bonding situation is depicted in Fig. 4 and details of

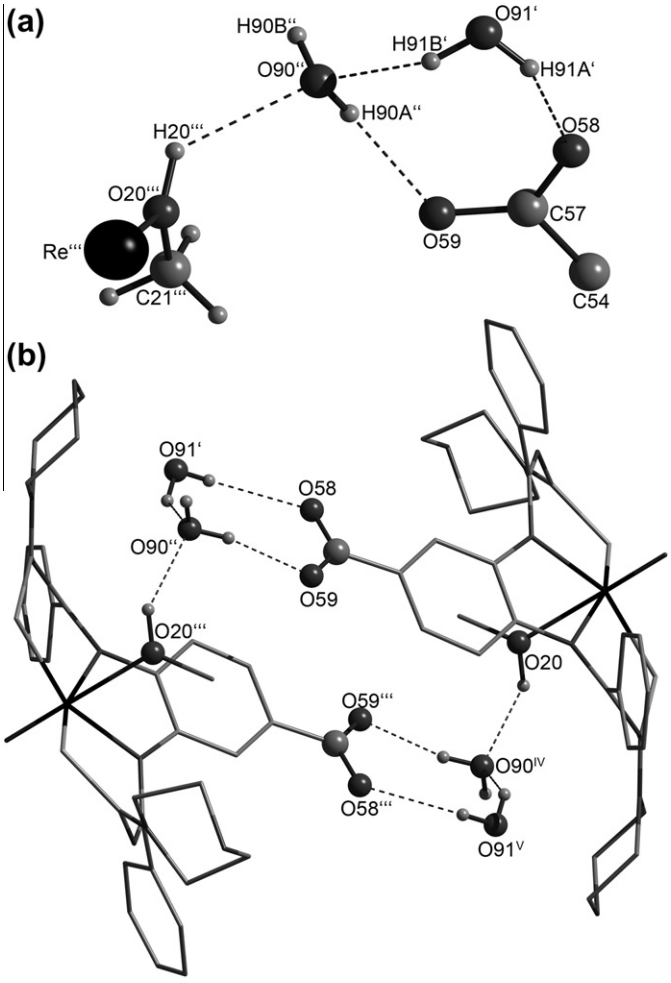


Fig. 4. Hydrogen bonds between [ReO(L^3)(MeOH)] [35] and the solvent water combining each two molecules of the complex to dimeric units. Symmetry operations: (′) −x, −y, 1 − z; (″) x − 1, y − 1, z; (‴) −x, −y, −z; (IV) 1 − x, 1 − y, −z; (V) x, y, 1 + z.

the established hydrogen bonds are given in Table 2. The hydrogen bonds organize each two complex molecules to dimeric units. Due to their deprotonation, the negatively charged carboxylate residues cannot undergo direct interactions, but by means of water molecules, which act as primary H atom donors for this bonding.

The spectroscopic data of [ReO(L^3)(MeOH] are in the accordance with the results of the X-ray diffraction study. The IR spectrum of the single crystals (measured in the ATR mode on a Nicolet-FT-IR 670 spectrometer) shows a strong band at 3407 cm^{-1}, which is caused by the co-crystallized water. The $\nu_{C=N}$ vibrations of the organic ligand can be identified at 1671 cm^{-1} and two strong bands at 1532 and 1517 cm^{-1} belong to the vibrations of the carboxylate anion. The $\nu_{Re=O}$ stretch appears as a band at 970 cm^{-1}. The ^{1}H NMR spectrum of [ReO(L^3)(MeOH)] in $CDCl_3$ shows a doublet at 6.54 ppm, which is caused by the hydrogen atom in meta position to the carboxylic function. All other aromatic signals can be found between 6.98 and 7.88 ppm. A broad multiplet between 3.86 and 4.51 ppm is assigned to the CH_2 groups of the morpholine substituents and is complex due to the hindered rotation of these residues. The ESI(+) spectrum of the substance shows no molecular peak [M+H]$^+$, but an intense peak at m/z = 817.1294, which corresponds to the [ReO(HL^3)]$^+$ fragment.

All complexes reported above have been prepared starting from the readily soluble complex (NBu_4)[$ReOCl_4$]. Analogous reactions with the common, but sparingly soluble oxidorhenium(V)

Table 2
Hydrogen bonding in [ReO(L^3)(MeOH)·2.6$CHCl_3$·2H_2O and [ReO(HL^3)(TFA)]·HTFA. For symmetry designators see Figs. 4 and 5.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
[ReO(L^3)(MeOH)·2.6$CHCl_3$·2H_2O				
O20‴–H20‴···O90‴	0.93	2.25	2.933(7)	129.9
O91′–H91A′···O58	0.85	2.324(11)	2.999(11)	136.7(4)
O91′–H91B′···O90″	0.85	2.23	2.9112(3)	137.361(6)
O90″–H90A″···O59	0.85	2.071(10)	2.888(10)	161.2(3)
[ReO(HL^3)(TFA)]·HTFA				
O58–H58···O59′	0.82	1.76	2.574(9)	172.8
O82″–H82″···O22	0.82	1.75	2.558(9)	167.2
O82″–H82″···F25	0.82	2.51	2.907(12)	111.2

precursor [$ReOCl_3(PPh_3)_2$] with H_2L^1 and H_2L^2 in refluxing CH_2Cl_2 or CH_3CN delivered almost insoluble red solids of unsatisfactory purity. Elemental analysis and IR spectra of the products confirm the presence of the organic ligand together with oxidorhenium(V) core(s). Most probably, the products represent mixtures of [ReO(L)Cl] complexes with mixtures of oligomeric compounds. Unfortunately, NMR or MS studies were not possible due to their low solubility. This is also the reason that we did not follow this synthetic approach further for the unsubstituted ligands H_2L^1 and H_2L^2.

In the case of the reaction of [$ReOCl_3(PPh_3)_2$] with H_3L^3, the product could be purified and isolated in crystalline form. Recrystallization of the initially also sparingly soluble red compound from trifluoroacetic acid (HTFA) gave red single crystals of the composition [ReO(HL^3)(TFA)]·HTFA, which were suitable for X-ray structure analysis. As in all previous examples, this complex also shows a distorted octahedral coordination around the rhenium atom, with an oxido and a trifluoroacetato ligand in trans-position to each other. The tetradentate organic ligand occupies the equatorial coordination plane of the molecule (Fig. 5a). An additional trifluoroacetic acid molecule is co-crystallized in the asymmetric unit and forms hydrogen bonds to the trifluoroacetato ligand.

The Re–O10 length of 1.665(5) Å is in the expected range for a rhenium–oxygen double bond. This bond exerts a strong structural trans influence which weakens the Re–O bond to the trifluoroacetato ligand (2.272(5) Å). The carboxylic group of the ligand $\{HL^3\}^{2-}$ is protonated in this complex, which can only partially be derived from a bond lengths consideration (C57–O58: 1.31(1) Å, C57–O59: 1.28(1) Å), but clearly be seen by the hydrogen bonding situation, which is shown in Fig. 5b. Two adjacent [ReO(HL^3)(TFA)] molecules are arranged to dimers via the hydrogen bonding of the carboxylic group. A comparison of the hydrogen bonds in [ReO(L^3)(MeOH)] and [ReO(HL^3)(TFA)] strongly indicate the different bonding

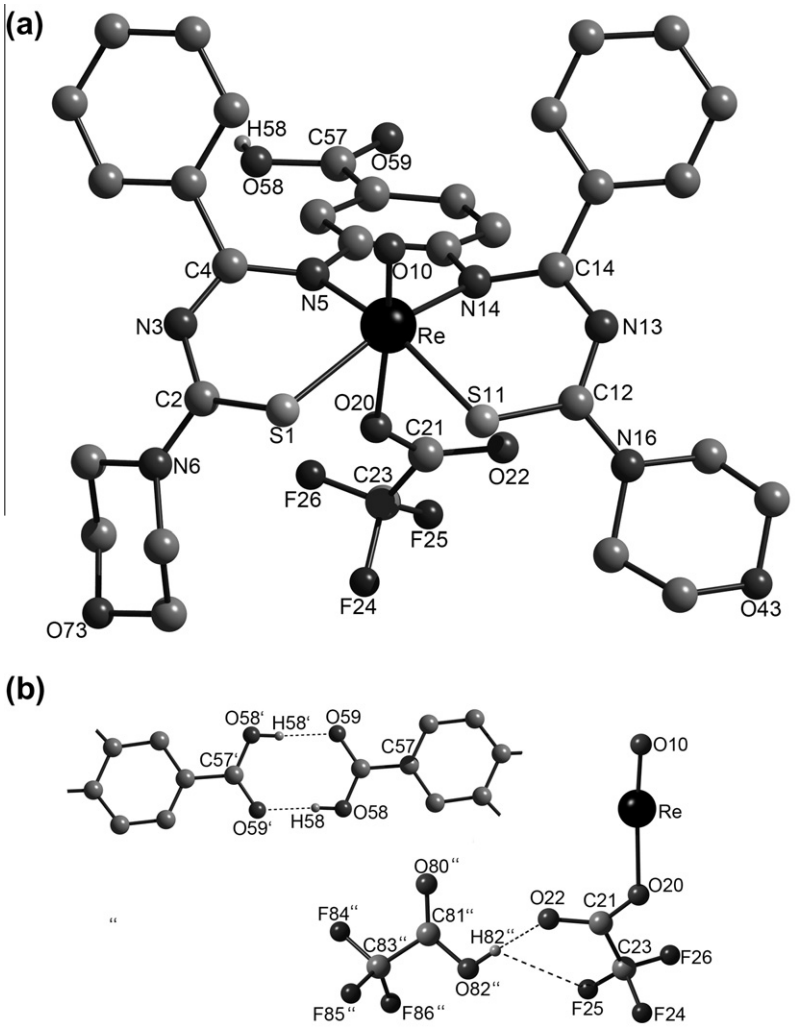


Fig. 5. Molecular structure [35] of [ReO(HL^3)(TFA)] (a) and hydrogen bonding in the solid state structure of [ReO(HL^3)(TFA)]·HTFA (b).

Table 3
X-ray structure data collection and refinement parameters.

	$[ReO(L^1)(OReO_3)]$	$[\{ReO(L^2)\}_2O]\cdot CH_2Cl_2$	$[ReO(L^3)(MeOH)]\cdot 2.6CHCl_3\cdot 2H_2O$	$[ReO(HL^3)(TFA)]\cdot HTFA$
Formula	$C_{30}H_{34}N_6O_5Re_2S_2$	$C_{61}H_{62}Cl_2N_{12}O_7Re_2S_4$	$C_{34.6}H_{39.6}Cl_{7.8}N_6O_8ReS_2$	$C_{35}H_{31}F_6N_6O_9ReS_2$
Formula weight	995.15	1646.77	1197.34	1043.99
Crystal system	monoclinic	tetragonal	triclinic	triclinic
a (Å)	14.109(1)	19.549(5)	12.246(1)	11.359(1)
b (Å)	11.160(1)	19.549(5)	13.8131)	12.148(1)
c (Å)	21.779(2)	17.943(5)	16.484(1)	16.022(2)
α (°)	90	90	108.88(1)	91.51(1)
β (°)	102.96(1)	90	106.59(1)	105.82(1)
γ (°)	90	90	98.26(1)	111.96(1)
V (Å^3)	3341.9(5)	6857(3)	2441.3(3)	1952.3(3)
Space group	$P2_1/n$	$P4_12_12$	$P\bar{1}$	$P\bar{1}$
Z	4	4	2	2
$D_{calc.}$ (g cm^{-3})	1.978	1.595	1.623	1.776
μ (mm^{-1})	7.410	3.785	3.056	3.309
No. of reflections	35020	7291	18340	20541
No. of independent	8954	5240	8557	10432
No. of parameters	434	404	546	532
R_1/wR_2	0.0441/0.0781	0.0463/0.0780	0.0703/0.16878	0.0503/0.1118
Goodness-of-fit (GOF) on F^2	0.924	0.950	0.975	0.863

modes of the carboxylic group of the organic ligand in these two complexes.

3. Conclusions

The tetradentate *SNNS* ligands under study are well suitable to form stable complexes with oxidorhenium(V) cores. They occupy the equatorial coordination spheres of the resulting complexes. Substitution in the molecular periphery allow the introduction of anchor groups for bioconjugation, which do not contribute to the coordination of the transition metal as has been demonstrated by an carboxylic group at the central phenyl ring of the ligand.

For reproducible syntheses of uniform rhenium (or technetium) compounds under conditions which are required for nuclear medical applications, however, the combination with oxidometal(V) cores seems to be inappropriate. The combination of the $\{MO\}^{3+}$ core with the tetradentate, binegative *SNNS* ligands obviously causes significant problems with the charge compensation in the formed complexes, particularly with the occupation of the sixth coordination site. This results in the formation of various complex species depending on the reaction conditions applied, including dimeric μ-oxo compounds and complexes with perrhenato ligands.

Such undesired side-reactions may be avoided by choosing a better appropriate metal core, such as the $\{M{\equiv}N\}^{2+}$ units (M = Re, Tc), which should be able to form neutral, five-coordinate rhenium or technetium complexes with the title ligands. Accordant studies are currently underway in our laboratories.

4. Experimental

4.1. Materials

All reagents used in this study were reagent grade and used without further purification. The syntheses of corresponding *N,N*-dialkylamino-*N′*-(thiocarbonyl)benzimidoyl chlorides followed the standard procedures [11,30,31]. $(NBu_4)[ReOCl_4]$ [32] and $[ReOCl_3(PPh_3)_2]$ [33] were prepared by published methods.

4.2. Physical measurements

Infrared spectra were measured from KBr pellets on a Shimadzu FT-IR-spectrometer or an Nicolet FT-IR 670 instrument between 400 and 4000 cm^{-1}. ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technologies). All MS results are given in the form: m/z, assignment. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus Vario EL elemental analyzer. The elemental analyses of the rhenium compounds showed systematically too low values for hydrogen and sometimes carbon (in some cases in a significant extent). This might be caused by an incomplete combustion of the metal compounds and/or hydride formation, and does not refer to impure samples. Similar findings have been observed for analogous oxorhenium(V) complexes with the same type of ligands before [13,19]. We left these values uncorrected. Additional proof for the identity of the products is given by high-resolution mass spectra for selected representatives. NMR-spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

4.3. Syntheses

4.3.1. H_2L^1 and H_2L^2

Solid thiocarbamoylbenzimidoyl chloride (5 mmol) was added to a stirred solution of *o*-phenylenediamine (252 mg, 2.5 mmol) and triethylamine (1.01 g, 10 mmol) in 10 mL of dry THF. The mixture was stirred for 4 h and then cooled to 0 °C. The formed precipitate was filtered off and the solvent was removed under vacuum. The resulting residue was recrystallized from diethyl ether.

H_2L^1: Yield: 815 mg (30%). *Anal.* Calc. for $C_{30}H_{36}N_6S_2$: C, 66.14; H, 6.66; N, 15.43; S, 11.77. Found: C, 66.01; H, 6.45; N, 15.29; S, 11.89%. IR (ν in cm^{-1}): 3055(w), 2927(m), 2860(w), 1640(vs), 1423(s), 1353(s), 1253(m), 1095(m), 1064(m), 995(m), 744(m), 694(s). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.32 (m, 12H, CH_3), 3.67 (m, 8H, NCH_2), 6.34 (d, br, 2H, C_6H_4), 6.56 (d, br, 2H, C_6H_4), 7.23 (t, J = 7.1 Hz, 4H, Ph), 7.48 (t, J = 7.2 Hz, 2H, Ph), 7.50 (d, J = 7.4 Hz, 4H, Ph).

H_2L^2: 1.57 g (55%). *Anal.* Calc. for $C_{30}H_{32}N_6O_2S_2$: C, 62.91; H, 5.63; N, 14.67; S, 11.20. Found: C, 63.10; H, 5.35; N, 14.16; S, 11.08%. IR (ν in cm^{-1}): 3417(m), 3335(m), 3209(m), 3060(w), 2962(m), 2912(w), 2858(s), 2731(w), 2599(m), 2495(m), 2380(w), 2337(w), 2052(w), 1963(w), 1674(w), 1624(s), 1569(w), 1423(s), 1350(m), 1276(s), 1226(s), 1110(s), 1064(m), 999(s), 925(w), 837(m), 748(s), 694(s). ^{1}H NMR ($CDCl_3$; δ, ppm): 3.66 (t, br, J = 4.8 Hz, 4H, NCH_2), 3.70 (t, br, J = 4.9 Hz, 4H, NCH_2), 4.02 (t, br, J = 4.8 Hz, 4H, OCH_2), 4.10 (t, br, J = 4.8 Hz, 4H, OCH_2), 6.90 (m, 2H, C_6H_4), 7.16–7.22 (m, 10H, Ph + C_6H_4), 7.31 (t, J = 7.8 Hz, 2H, Ph).

4.3.2. $[Et_3NH][H_2L^3]$

Solid morpholinylthiocarbonylbenzimidoyl chloride (4 g, 15 mmol) was added to a stirred solution of 3,4-diaminobenzoic

acid (1.13 g, 7.5 mmol) and triethylamine (3.03 g, 30 mmol) in 20 mL of dry THF. The mixture was stirred for 4 h and then cooled to 0 °C. The formed precipitate was filtered off and the solvent was removed under vacuum. The resulting residue was recrystallized from diethyl ether. Yield: 5.19 g (88%). *Anal.* Calc. for $C_{37}H_{47}N_7O_4S_2$: C, 61.90; H, 6.60; N, 13.66; S, 8.93. Found: C, 59.99; H, 6.59; N, 13.15; S, 8.89%. IR (ν in cm^{-1}): 3321(m), 3205(m), 2974(s), 2854(s), 2627(w), 2496(m), 1701(m), 1697(w), 1597(s), 1470(m), 1427(m), 1280(s), 1223(s), 1026(s), 837(w), 783(s), 698(s). ^1H NMR ($CDCl_3$; δ, ppm): 1.27 (t, J = 7.3 Hz, 9H, CH_3), 3.05 (q, J = 7.3 Hz, 6H, ethyl-CH_2), 3.68–3.77 (m, 8H, morph-NCH_2), 3.97–4.29 (m, 8H, OCH_2), 6.67 (d, J = 8.24 Hz, 1H, C_6H_3), 7.15–8.32 (m, 12H, Ph + C_6H_3), 10.81(s, br, 1H, NH). ESI(+) TOF-MS (m/z): 102.1288 ($[Et_3NH]^+$, Calc. 102.1283), 617.2014 ($[H_4L^3]^+$, Calc. 617.2004). ESI(−) TOF-MS (m/z): 615.1877 ($[H_2L^3]^-$, Calc. 615.1848).

4.3.3. [ReO(L^1)($OReO_3$)]

H_2L^1 (54 mg, 0.1 mmol) and three drops of NEt_3 were added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in MeOH (3 mL). This solution was heated under reflux for 30 min and finally the solvent was removed under vacuum. The residue was dissolved in acetone. The resulting clear red solution was slowly evaporated at room temperature to give red crystals. Yield: 15 mg (15%). *Anal.* Calc. for $C_{30}H_{34}N_6O_5S_2Re_2$: C, 36.21; H, 3.44; N, 8.44; S, 6.44. Found: C, 36.51; H, 3.22; N, 8.59; S, 6.63%. IR (ν in cm^{-1}): 3055(w), 2970(w), 2936(w), 1543(vs), 1477(s), 1443(m), 1346(s), 1280(m), 1242(m), 1141(m), 1076(m), 983(m), 921(s), 875(s), 767(m). ^1H NMR (acetone-d_6; δ, ppm): 1.43 (t, J = 7.2 Hz, 6H, CH_3), 1.49 (t, J = 7.1 Hz, 6H, CH_3), 4.05 (m, 4H, CH_2) 4.37 (m, 2H, CH_2), 4.45 (m, 2H, CH_2), 6.53 (m, 2H, C_6H_4), 6.60 (m, 2H, C_6H_4), 7.52 (t, J = 7.2 Hz, 4H, Ph), 7.53 (d, J = 7.1 Hz, 4H, Ph), 7.58 (t, J = 7.2 Hz, 2H, Ph). FAB^+ MS (m/z): 745.4 $[M-ReO_4^-]^+$.

4.3.4. [{ReO(L^2)}O]

Solid H_2L^2 (57 mg, 0.1 mmol) was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in MeOH (3 mL). The reaction mixture was heated under reflux for 5 min, before 3 drops of Et_3N were added. The heating was continued for 30 min and the solvent was removed under vacuum. The resulting residue was recrystallized from a CH_2Cl_2/acetone mixture giving red crystals. Yield: 54 mg (69%). *Anal.* Calc. for $C_{60}H_{60}N_{12}O_7S_4Re_2$: C, 46.14; H, 3.87; N, 10.76; S, 8.21. Found: C, 46.12; H, 3.95; N, 10.51; S, 8.06%. IR (ν in cm^{-1}): 3055(w), 2962(w), 2916(w), 2854(w), 1527(vs), 1477(vs), 1438(m), 1420(vs), 1361(s), 1265(m), 1226(m), 1172(w), 1114(m), 1026(m), 941(w), 767(m), 744(w), 694 (w). ^1H NMR ($CDCl_3$; δ, ppm): 3.5–3.7 (m, br, 4H, NCH_2), 3.8–4.0 (m, br, 4H, NCH_2), 4.1–4.3 (m, br, 4H, OCH_2), 4.64 (d, br, 2H, OCH_2), 4.80 (d, br, 2H, OCH_2), 5.95 (d, J = 8.3 Hz, 1H, CH_2), 6.22 (d, J = 7.8 Hz, 1H, C_6H_4), 6.37 (t, J = 7.7 Hz, 1H, C_6H_4), 6.47 (t, J = 7.7 Hz, 1H, C_6H_4), 7.11 (m, 4H, Ph), 7.29 (m, 4H, Ph), 7.53 (d, J = 7.1 Hz, 2H, Ph). FAB^+ MS (m/z): 790.8 $[ReO(H_2O)(L^2)]^+$, 774.9 $[ReO(L^2)]^+$.

4.3.5. [ReO(L^3)(MeOH)]

$(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) was dissolved in 20 mL of a mixture of chloroform and methanol (1:1). A solution of 79.1 mg $(Et_3NH)[H_2L^3]$ (0.11 mmol) in ca. 2 mL methanol was added. The reaction mixture was stirred for about 30 min and left to evaporate. After 24 h, orange-red crystals were isolated. Yield: 64 mg (75%). *Anal.* Calc. for $C_{32}H_{33}N_6O_6S_2Re{\cdot}2H_2O{\cdot}2CHCl_3$: 36.37; H, 3.50; N, 7.49; S, 5.71. Found (after slight drying): C, 37.12; H, 3.45; N, 8.01; S, 6.02%. IR (ν in cm^{-1}): 3600(w), 3407(w), 3362(w), 2967(s), 2928(w), 2888(w), 2850(m), 2615(m), 1596(m), 1581(m), 1532(s), 1517(s), 1493(w), 1448(m), 1438(m), 1381(w), 1373(w), 1351(s), 1301(s), 1262(s), 1226(s), 1183(m), 1164(w), 1136(w), 1111(s), 1080(w), 1062(w), 1024(s), 978(s), 970(s), 963(s), 921(s), 896(s), 881(s), 822(s). ^1H NMR ($CDCl_3$; δ, ppm): 3.11 (s, 3H, OCH_3), 3.37 (s, br, 1H, OH), 3.86–3.97 (m, 8H, OCH_2), 4.25–4.57 (m, 8H, NCH_2), 6.54 (d, J = 8.3 Hz, 1H, C_6H_3), 6.98–7.88 (m, 12H, Ph + C_6H_3). ESI TOF(+) (m/z): 817.1294 $[M-MeO^-]^+$ (Calc. 817.1276).

4.3.6. [ReO(HL^3)(TFA)]·HTFA

$[ReOCl_3(PPh_3)_2]$ (83 mg, 0.1 mmol) was suspended in 5 mL THF. Solid $[Et_3NH][H_2L^3]$ (0.11 mmol) and 3 drops of NEt_3 were added. The suspension was stirred for 4 h at room temperature. The resulting red precipitate was filtered off, washed with acetone and diethyl ether and redissolved in pure trifluoroacetic acid (HTFA). Orange-red crystals were obtained by slow evaporation of this solution. Yield: 23 mg (22 %). IR (ν in cm^{-1}): 3367(w), 2995(m), 2809(w), 2707(m), 2517(m), 2359(w), 1775(w), 1759(w), 1730(w), 1673(s), 1634(m), 1597(w), 1582(w), 1528(s), 1492(m), 1480(w), 1465(w), 1446(m), 1428(s), 1353(s), 1309(s), 1274(s), 1262(m), 1196(s), 1174(s), 1139(s), 1116(m), 1064(w), 1025(m), 966(m), 799(m), 769(m), 720(m), 672(m), 649(w), 597(w), 533(w). ^1H NMR ($CDCl_3$; δ, ppm): 3.68–3.99 (m, 8H, OCH_2), 4.22–4.64 (m, 8H, NCH_2), 6.51 (d, J = 8.7 Hz, 1H, C_6H_3), 6.95–8.06 (m, 12H, Ph + C_6H_3), 9.17 (s, br, 1H, COOH), 11.49 (s, br, 1H, COOH). ESI TOF(+) (m/z): 817.1299 $[M-TFA^-]^+$ (Calc. 817.1276).

4.4. X-ray crystallography

The intensities for the X-ray determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation (λ = 0.71073 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS and SHELXL [34]. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of SHELXL.

More details on data collections and structure calculations are contained in Table 3. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre.

Appendix A. Supplementary data

CCDC 881796, 881797, 881798 and 881799 contain the supplementary crystallographic data for [ReO(L^1)($OReO_3$)], [{ReO(L^2)}$_2$O], [ReO(L^3)(MeOH)] and [ReO(L^3)(TFA)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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