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Oxorhenium(V) complexes containing tridentate Schiff-base and monothiol coligands

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Abstract

The reaction of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ with the tridentate Schiff-base $[HOC_6H_4C(H)NC_6H_4SH]$ allows for the isolation of $[ReOBr\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}]$ (**1**). The reaction of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ with $[HOC_6H_4C(H)NC_6H_4SH]$ and the appropriate benzenethiol ($C_6H_4X-4-SH$) where $X=H, Br, Cl, F$, and OCH_3 in methanol–acetonitrile treated with triethylamine has led to the isolation of a series of rhenium complexes of the type $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4X-4-S)]$ ($X=H$ (**2**), Br (**3**), Cl (**4**), F (**5**), and OCH_3 (**6**)). Likewise, under similar reaction conditions, the use of benzylmercaptan ligands of the type ($C_6H_4X-4-CH_2SH$) where $X=H, Cl, F$, and OCH_3 has led to the isolation of a series of rhenium complexes of the type $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4X-4-CH_2S)]$ ($X=H$ (**7**), Cl (**8**), F (**9**), and OCH_3 (**10**)). The incorporation of the appropriate amine functionality into the substituent R of the monodentate ligand allows for the isolation of a cationic oxorhenium(V) species, namely, $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_5H_4NH-2-S)][Br]$ (**11**).

Keywords

Oxorhenium(V) complexes; Tridentate Schiff-base; Monothiol coligands

1. Introduction

A major focus of the contemporary interest in the chemistries of the Group VII congeners technetium and rhenium reflects the applications of ^{99m}Tc and ^{186}Re or ^{188}Re in radiodiagnosis and radiotherapy, respectively [1–4]. The nuclear properties of ^{99m}Tc ($t_{1/2}=6h$, $\gamma=140$ keV) are ideal for diagnostic imaging, while the β -emitting isotopes ^{186}Re and ^{188}Re ($t_{1/2}=90.64$ h, $E_{max}=1.1$ MeV, $t_{1/2}=17$ h, $E_{max}=2.1$ MeV, respectively) are promising candidates for therapeutic applications [5]. One successful approach to the development of diagnostic imaging agents of technetium and to potential therapeutic reagents based on rhenium has exploited Schiff-base ligands set to stabilize the $[MO]^{3+}$ core for $M=Tc(V)$ and $Re(V)$ [6–19]. Schiff-base ligands offer a considerable versatility in their substituent groups, and thus the possibility exists for designing technetium and rhenium complexes with useful biological properties [7].

The first rhenium complexes with Schiff-base ligands were reported by Middleton et al. in 1979 [6]. Since then polydentate Schiff-base complexes have been extensively explored for the development of both technetium and rhenium coordination chemistry with radiopharmaceutical applications [6–19]. Research groups have primarily focused their

attention on the chemistry of *O,N,N,O*-tetradentate Schiff-base ligands derived from salicylaldehyde and diamines (salenes) [6-12], as well as bi- and tridentate oxygen, nitrogen, and sulfur containing Schiff-base complexes of rhenium and technetium [13-19].

Polydentate Schiff-base ligands appear to be suitable systems to stabilize and surround the $[MO]^{3+}$ core for $M=Tc(V)$ and $Re(V)$ [10]. Several X-ray structures of technetium and rhenium complexes with Schiff-base ligands have been reported, mainly containing the $[MO]^{3+}$ core ($M=Tc(V)$ or $Re(V)$) [6-19]. The geometry of these complexes depends solely on the nature of the ligand, namely, the number and type of coordinating atoms, and the chain length between the coordinating groups. Five-coordinate examples of complexes containing the TcO^{3+} core in a square-pyramidal configuration include $[TcOCl(OPhsal)]$ ($OPhsal=N$ -(2-oxidophenyl) salicylideneimine) [16] and $[TcOCl(SPhsal)]$ ($SPhsal=N$ -(2-sulfidophenyl) salicylideneimine) [13]. Six-coordinate compounds containing the TcO^{3+} core in a distorted octahedral environment are represented by $[TcO(OPhsal)(8\text{-quinolate})]$ [17] and $[TcOCl(Phsal)_2]$ ($Phsal$ =phenylsalicylideneimine) [19], while $\mu\text{-O}[TcO(sal_2pn)]_2$ ($sal_2pn=N,N'$ -propane-1,3-bis(salicylideneimine) [7] is an example of a six-coordinate compound containing the $Tc_2O_3^{4+}$ core and possessing a quasi-linear $O=Tc-O-Tc=O$ bridge.

As an extension of this chemistry, Spies and co-workers determined that mononuclear, neutral, and low molecular weight technetium and rhenium complexes of the type $MO(SXS)(SR)$ for $M=Tc(V)$ or $Re(V)$ were attainable by the reaction of tridentate dithiol ligands $HSXSH$ ($X=S, O$) and monodentate thiol ligands $R-SH$ (thiophenols, aliphatic thioles, etc.) with starting materials containing the $MO(V)$ [$M=Tc, Re$] core [20,21]. Using this methodology, $Tc(V)$ compounds based on the '3+1' donor ligand design based on tridentate Schiff-bases in combination with monothiols were synthesized [15,18]. Since then a variety of other groups have continued to exploit the full range of $Tc(V)$ compounds involving bi- and tridentate Schiff-base ligands [13-19].

In an effort to expand '3+1' chemistry to the oxorhenium core, our work has concentrated on the reactions of the potentially tridentate Schiff-base $[HOC_6H_4-C(H)NC_6H_4SH]$ with the recently described $[n(C_4H_9)_4N][ReOBr_4(OPPh_3)]$, so as to prepare families of compounds with mixed thiol ligands, starting with the systematic exploration of the *para*-substituted benzenethiol and benzylmercaptan series. This study continues our development of the coordination chemistry of the Group VII metal rhenium [22-26] in order to provide new materials for radiolabeling of chemotactic peptides [27]. We report the synthesis and structural characterization of an intermediate oxorhenium compound, namely, $[ReOBr\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}]$ (**1**), a series of oxorhenium '3+1' benzenethiolate complexes $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4X-4-S)]$ ($X=H$ (**2**), Br (**3**), Cl (**4**), F (**5**), and OCH_3 (**6**)), as well as a series of benzylmercaptan complexes $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1C_6H_4X-4-CH_2S)]$ ($X=H$ (**7**), Cl (**8**), F (**9**), and OCH_3 (**10**)), and an example of a cationic oxorhenium(V) species, $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1C_5H_4NH-2-S)][Br]$ (**11**).

2. Experimental

2.1. General considerations

NMR spectra were recorded on a Bruker DPX 300 (1H 300.10 MHz) spectrometer in CD_2Cl_2 (δ 5.32). IR spectra were recorded as KBr discs with a Perkin-Elmer Series 1600 FT IR. Elemental analysis for carbon, hydrogen, and nitrogen were carried out by Oneida Research Services, Whitesboro, NY. Tetrabutylammonium perrhenate (Aldrich), triethylamine (Aldrich), salicylaldehyde (Aldrich), 2-aminothiophenol (Aldrich), benzenethiol (Aldrich), 4-bromobenzenethiol (Aldrich), 4-chlorobenzenethiol (Aldrich), 4-fluorobenzenethiol (Aldrich), 4-methoxybenzenethiol (Aldrich), benzylmercaptan (Aldrich), 4-chlorobenzyl mercaptan (Aldrich), 2-mercaptopyridine (Aldrich), 4-fluorobenzyl mercaptan (Lancaster), 4-

methoxybenzyl mercaptan (Lancaster) were used as received without further purification. All other solvents and reagents were purchased from Aldrich and used as received, unless otherwise stated. The $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ [24] and *N*-(2-mercaptophenyl)salicylideneimine [13] were synthesized according to published procedures.

2.2. Syntheses

2.2.1. Preparation of $[ReOBr\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}](1)$ —A solution of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ (0.05 g, 0.0493 mmol) in a mixture of 10 ml of chloroform and 1 ml of methanol was placed in an ice-bath. To this solution was added dropwise a 5 ml chloroform solution of $[HOC_6H_4C(H)NC_6H_4SH]$ (0.010 g, 0.0445 mmol). The solution color changed from pink to orange upon addition. The solution was stirred for an additional 30 min and subsequently evaporated to dryness. The resulting orange residue was dissolved in methylene chloride and layered with pentane to form X-ray crystals of **1** (yield: 0.006 g, 26.09%). IR (KBr, cm^{-1}): 1654 (m), 1608 (s), 1545 (s), 1507 (w), 1421 (m), 1259 (w), 968 (s), 850 (w). 1H NMR (CD_2Cl_2 , ppm): 7.15–8.07 (mm, 8H), 9.53 (s, 1H).

2.2.2. General procedure for the preparation of $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4X-4-S)]$ where $X=H$ (2**), **Br** (**3**), **Cl** (**4**), **F** (**5**), and **OCH₃** (**6**)**—A solution of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ (0.05 g, 0.0493 mmol) in 2 ml of methanol was placed in an ice-bath. To this solution was added dropwise with stirring a 2 ml acetonitrile solution consisting of 1 equiv. of $[HOC_6H_4C(H)NC_6H_4SH]$ (11.3 mg, 0.0493 mmol) and 1 equiv. of the benzenethiol $[C_6H_4X-4-S]$ ($X=H$, **Br**, **Cl**, **F**, and **OCH₃**) (0.0493 mmol). A drop of triethylamine (0.010 g, 0.099 mmol) was then added and the reaction mixture changed from pink to orange–brown immediately, and an orange–brown precipitate was deposited. After stirring for 20 min the solid material was filtered and allowed to air dry. X-ray quality crystals for compounds **3**, **5**, and **6** were grown by slow diffusion of pentane in a solution of the compounds in methylene chloride.

2.2.2.1. $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_5-4-S)]$ (2**):** (Yield: 0.015 g, 55.6%). IR (KBr, cm^{-1}): 1654 (m), 1607 (s), 1560 (s), 1534 (m), 1508 (w), 1438 (m), 1262 (w), 970 (s), 862 (w). 1H NMR (CD_2Cl_2 , ppm): 7.15–8.07 (mm, 13H), 9.53 (s, 1H). *Anal.* Calc. for $C_{19}H_{14}NO_2S_2Re$ (mol. wt. 538.65): C, 42.37; H, 2.62; N, 2.60. Found: C, 42.58; H, 2.60; N, 2.81%.

2.2.2.2. $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4Br-4-S)]$ (3**):** (Yield: 0.012 g, 40.0%). IR (KBr, cm^{-1}): 1654 (m), 1606 (s), 1560 (s), 1535 (m), 1508 (w), 1432 (m), 1228 (w), 968 (s), 864 (w). 1H NMR (CD_2Cl_2 , ppm): 7.18–8.08 (mm, 12H), 9.54 (s, 1H). *Anal.* Calc. for $C_{19}H_{13}NO_2S_2BrRe$ (mol. wt. 617.53): C, 36.96; H, 2.12; N, 2.27. Found: C, 37.25; H, 2.31; N, 2.18%.

2.2.2.3. $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4Cl-4-S)]$ (4**):** (Yield: 0.012 g, 42.9%). IR (KBr, cm^{-1}): 1654 (m), 1606 (s), 1560 (s), 1535 (m), 1508 (w), 1438 (m), 1230 (w), 968 (s), 864 (w). 1H NMR (CD_2Cl_2 , ppm): 7.20–8.10 (mm, 12H), 9.53 (s, 1H). *Anal.* Calc. for $C_{19}H_{13}NO_2S_2ClRe$ (mol. wt. 573.09): C, 39.82; H, 2.29; N, 2.44. Found: C, 40.03; H, 2.56; N, 2.17%.

2.2.2.4. $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4F-4-S)]$ (5**):** (Yield: 0.012 g, 44.4%). IR (KBr, cm^{-1}): 1654 (m), 1606 (s), 1560 (s), 1536 (m), 1508 (w), 1432 (m), 1225 (w), 970 (s), 864 (w). 1H NMR (CD_2Cl_2 , ppm): 7.20–8.10 (mm, 12H), 9.53 (s, 1H). *Anal.* Calc. for $C_{19}H_{13}NO_2S_2FRe$ (mol. wt. 556.62): C, 41.00; H, 2.35; N, 2.52. Found: C, 41.33; H, 2.64; N, 2.10%.

2.2.2.5. $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{OCH}_3\text{-4-S})]$ (6): (Yield: 0.020 g, 71.4%). IR (KBr, cm^{-1}): 1654 (m), 1606 (s), 1560 (s), 1535 (m), 1508 (w), 1438 (m), 1239 (w), 968 (s), 864 (w). ^1H NMR (CD_2Cl_2 , ppm): 3.90 (s, 3H), 7.05–8.08 (m, 12H), 9.52 (s, 1H). *Anal.* Calc. for $\text{C}_{20}\text{H}_{16}\text{NO}_3\text{S}_2\text{Re}$ (mol. wt. 568.66): C, 42.24; H, 2.84; N, 2.46. Found: C, 42.13; H, 2.61; N, 2.19%.

2.2.3. General procedure for the preparation of $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{X-4-CH}_2\text{S})]$ where X=H (7), Cl (8), F (9), and OCH_3 (10)—A solution of $[\text{n-(C}_4\text{H}_9)_4\text{N}][\text{ReOBr}_4(\text{OPPh}_3)]$ (0.05 g, 0.0493 mmol) in 2 ml of methanol was placed in an ice-bath. To this solution was added dropwise with stirring a 2 ml acetonitrile solution consisting of 1 equiv. of $[\text{HOC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{SH}]$ (11.3 mg, 0.0493 mmol) and 1 equiv. of the benzylmercaptan $[\text{C}_6\text{H}_4\text{X-4-CH}_2\text{S}]$ (X=H, Cl, F, and OCH_3) (0.0493 mmol). A drop of triethylamine (0.010 g, 0.099 mmol) was then added and the reaction mixture changed from pink to orange–brown immediately, and an orange–brown precipitate was deposited. After stirring for 20 min. the solid material was filtered and allowed to air dry. X-ray quality crystals for compounds 7–9 were grown by slow diffusion of pentane in a solution of the compounds in methylene chloride.

2.2.3.1. $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_5\text{-4-CH}_2\text{S})]$ (7): (Yield: 0.010 g, 37.0%). IR (KBr, cm^{-1}): 1654 (m), 1607 (s), 1560 (s), 1540 (m), 1508 (w), 1438 (m), 1292 (w), 969 (s), 862 (w). ^1H NMR (CD_2Cl_2 , ppm): 5.03 (s, 2H), 7.27–8.05 (m, 13H), 9.53 (s, 1H). *Anal.* Calc. for $\text{C}_{20}\text{H}_{16}\text{NO}_2\text{S}_2\text{Re}$ (mol. wt. 552.66): C, 43.47; H, 2.92; N, 2.53. Found: C, 43.53; H, 2.85; N, 2.57%.

2.2.3.2. $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{Cl-4-CH}_2\text{S})]$ (8): (Yield: 0.010 g, 34.5%). IR (KBr, cm^{-1}): 1654 (m), 1608 (s), 1560 (s), 1539 (m), 1508 (w), 1428 (m), 1225 (w), 972 (s), 857 (w).

^1H NMR (CD_2Cl_2 , ppm): 5.02 (s, 2H), 7.20–8.06 (m, 12H), 9.54 (s, 1H). *Anal.* Calc. for $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{S}_2\text{ClRe}$ (mol. wt. 587.10): C, 40.92; H, 2.58; N, 2.39. Found: C, 40.23; H, 2.39; N, 2.18%.

2.2.3.3. $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{F-4-CH}_2\text{S})]$ (9): (Yield: 0.011 g, 39.3%). IR (KBr, cm^{-1}): 1654 (m), 1608 (s), 1560 (s), 1539 (m), 1506 (w), 1433 (m), 1221 (w), 968 (s), 862 (w). ^1H NMR (CD_2Cl_2 , ppm): 5.04 (s, 2H), 6.98–8.06 (m, 12H), 9.54 (s, 1H). *Anal.* Calc. for $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{S}_2\text{FRe}$ (mol. wt. 570.65): C, 42.10; H, 2.65; N, 2.45. Found: C, 41.93; H, 2.77; N, 2.60%.

2.2.3.4. $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{OCH}_3\text{-4-CH}_2\text{S})]$ (10): (Yield: 0.018 g, 62.1%). IR (KBr, cm^{-1}): 1654 (m), 1607 (s), 1560 (s), 1536 (m), 1509 (w), 1438 (m), 1247 (w), 966 (s), 864 (w). ^1H NMR (CD_2Cl_2 , ppm): 3.77 (s, 3H), 5.02 (s, 2H), 6.86–8.05 (m, 12H), 9.53 (s, 1H). *Anal.* Calc. for $\text{C}_{21}\text{H}_{18}\text{NO}_3\text{S}_2\text{Re}$ (mol. wt. 582.70): C, 43.29; H, 3.11; N, 2.40. Found: C, 43.58; H, 3.44; N, 2.15%.

2.2.4. $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_5\text{H}_4\text{NH-2-S})][\text{Br}]\cdot\text{CH}_2\text{Cl}_2$ (11)—A solution of $[\text{n-(C}_4\text{H}_9)_4\text{N}][\text{ReOBr}_4(\text{OPPh}_3)]$ (0.050 g, 0.0493 mmol) in 8 ml of chloroform was placed in an ice-bath. To this solution was added dropwise with stirring a solution of 2-mercaptopyridine (5.48 mg, 0.0493 mmol) and $[\text{HOC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{SH}]$ (11.3 mg, 0.0493 mmol) in 2 ml of methanol. The solution was stirred for an additional 30 min, and subsequently evaporated to dryness. The red residue was dissolved in methylene chloride and layered with diethyl ether to form crystals of **11** (0.014 g, 40.0%). IR (KBr, cm^{-1}): 1654 (m), 1604 (s), 1588 (s), 1533 (m), 1507 (w), 1436 (m), 1268 (w), 978 (s), 856 (w). ^1H NMR (CD_2Cl_2 , ppm): 6.80–

8.22 (mm, 13H), 9.75 (s, 1H). *Anal.* Calc. for $C_{19}H_{16}N_2O_2S_2BrCl_2Re$ (mol. wt. 705.47): C, 32.35; H, 2.29; N, 3.97. Found: C, 32.01; H, 2.73; N, 3.85%.

2.3. X-ray crystallography

All data were collected on a Bruker SMART diffractometer system using graphite-monochromated Mo $K\alpha$ radiation ($\lambda(Mo\ K\alpha)=0.71073\ \text{\AA}$). All data collections were carried out at low temperature (85–94 K). The crystal parameters and other experimental details of the data collections are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the Supporting Information. The structures were solved by direct methods [28]. Neutral atom scattering factors were taken from Cromer and Waber [29] and anomalous dispersion corrections were taken from those of Creagh and McAuley [30]. All calculations were performed using *SHELXTL* [28]. Non-hydrogen atoms were refined anisotropically. No anomalies were encountered in the refinements of any of the structures.

3. Results and discussion

The choice of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ as starting material was predicted on the ease of substitution of the bromine ligands by a variety of ligand donors, as well as its potential for clinical applications. However, the relatively involved synthesis and low yield of this compound indicate that this material may not prove viable for radiopharmaceutical use. Furthermore, the more commonly employed oxorhenium(V)-halide starting material $[ReOCl_4]^-$ is extremely moisture sensitive and is also unlikely to be useful in clinical application. The IR spectrum of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ displays $\nu(C-H)$ for the $[n-(C_4H_9)_4N]^+$ cation at 2961 and 2872 cm^{-1} , $\nu(C-C)$ at 1466 cm^{-1} , and a strong band assigned to $\nu(Re-O)$ at 993 cm^{-1} . The pink solid is indefinitely air- and moisture-stable making it suitable for probing the reactivities of a variety of ligand types.

The synthesis of $[ReOBr\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}]$ employs the route of Fietz et al. [31], but instead of using $[ReOCl_4]^-$ the less moisture sensitive $[ReOBr_4-(OPPh_3)]^-$ was used. The starting material was placed in an ice-bath to prevent possible dimerization. The *O,N,S*-tridentate Schiff-base was added dropwise in 5 ml of chloroform over a period of 20 min. The orange solution was stirred in the ice-bath for an additional 30 min at which time it was vacuumed down to an orange residue. The residue was dissolved in methylene chloride and layered with pentane to produce crystalline $[ReOBr\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}]$ (**1**) (0.006 g, 26.09%). The IR spectrum of **1** is dominated by strong peaks at 964 and 1608 cm^{-1} which can be attributed to $\nu(Re=O)$ and $\nu(N=C)$, respectively. The 1H NMR spectrum contains a series of multiplets ranging from 7.15 to 8.07 ppm assignable to the aromatic protons comprising the backbone of the ligand; however, individual assignments of the resonances are tenuous at best due to the multiplicity of the peaks. On the other hand, the singlet integrating to one proton at 9.53 ppm is easily assigned to the imine proton of the ligand, and is in agreement with chemical shifts reported by others [13].

Although compounds **2–10** may be prepared by reacting the precursor, $[ReOBr\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}]$, with an excess of the appropriate ligand in acetonitrile, a methodology demonstrated by several groups [20,21,24–26], the relatively low yield of the isolated intermediate makes this a less than ideal synthetic route. However, improved yields of complexes **2–10** may be prepared in one step from the reaction of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ with a mixture of the appropriate tridentate and monodentate thiolate ligands. The syntheses of compounds $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4X-4-S)]$ ($X=H$ (**2**), Br (**3**), Cl (**4**), F (**5**), and OCH_3 (**6**)), as well as $[ReO\{\eta^3-(OC_6H_4C(H)NC_6H_4S)\}(\eta^1-C_6H_4X-4-CH_2S)]$ ($X=H$ (**7**), Cl (**8**), F (**9**), and OCH_3 (**10**)) employs the route by Spies et al. [21]. The addition of a 1:1 molar ratio of *O,N,S* Schiff-base and the substituted benzenethiol or benzylmercaptan in acetonitrile to a stirred solution of $[n-(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ in

methanol at 0°C, followed by the addition of excess triethylamine, resulted in a color change from the characteristic pink of the starting material to orange–brown. After stirring for 20 min, air-stable orange–brown precipitates in yields of 34 to 71% were isolated. The compounds are also accessible by reacting $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with equimolar amounts of the monodentate and tridentate ligands in chloroform. In this case the solution mixture must be heated briefly to complete the reaction in an appropriate time frame. However, the yields obtained by this synthetic method were much lower than the reported yields for the ligand-exchange reaction with $[\text{ReOBr}_4(\text{OPPh}_3)]^-$.

The infrared spectra of the products **1–10** displayed characteristically sharp $\nu(\text{Re}=\text{O})$ stretches from 966 to 972 cm^{-1} . The remainder of the spectra were dominated by $\nu(\text{C}=\text{C})$ stretching between 1400 and 1600 cm^{-1} and $\nu(\text{N}=\text{C})$ stretching ranging from 1606 to 1608 cm^{-1} . The ^1H NMR spectra displayed resonances assigned to aromatic protons from approximately 6.89 to 8.10 ppm, and a single resonance at approximately 9.53 ppm assigned to the imine proton. The monodentate benzylmercaptans displayed methylene protons at approximately 5.03 ppm as a single peak, as anticipated from Sadtler spectra [32]. The ^1H NMR of $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{OCH}_3\text{-4-S})]$ (**6**) and $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{OCH}_3\text{-4-CH}_2\text{S})]$ (**10**) exhibited an additional singlet at approximately 3.90 and 3.77 ppm, respectively, which are attributed to the three protons of the methoxy group.

The reaction of $[\text{n-(C}_4\text{H}_9)_4\text{N}][\text{ReOBr}_4(\text{OPPh}_3)]$ with $[\text{HOC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{SH}]$ and 2-mercaptopyridine yields **11** as red crystals. Compound **11** is a cationic rhenium(V) complex, charge balanced by a cocrystallizing Br^- , which originates from the $[\text{n-(C}_4\text{H}_9)_4\text{N}][\text{ReOBr}_4(\text{OPPh}_3)]$ starting material. The monodentate 2-mercaptopyridine ligand is clearly protonated on the pyridyl-nitrogen which is evident in the X-ray crystal-lography (vide infra). The infrared spectrum of **11** exhibited a strong sharp peak at 978 cm^{-1} , characteristic of $\nu(\text{Re}=\text{O})$ and a peak at 1604 cm^{-1} , which can be attributed to $\nu(\text{N}=\text{C})$. The complexity of peaks ranging from 6.80 to 8.22 ppm in the ^1H NMR spectrum did not allow direct assignment of the pyridyl N–H proton. However, the fact that these peaks integrate to 13 protons supports previous evidence that the pyridyl nitrogen is indeed protonated. Upon exchange studies with D_2O the peaks integrated to 12 protons, confirming the presence of an exchangeable site.

As shown in Fig. 1, the structure of $[\text{ReOBr}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}]$ is distorted square-pyramidal, the prototypical geometry encountered with the $[\text{MO}]^{3+}$ core for $\text{M}=\text{Tc(V)}$ and Re(V) . The structure consists of the *O,N,S*-tridentate Schiff-base ligand coordinated through an oxygen, nitrogen, and sulfur atom in the equatorial positions, a bromine ligand in the remaining equatorial position, and an oxo ligand in the axial site. The $\text{Re}=\text{O}$ bond length is found to be 1.67 Å. The structure of **1** is reminiscent of that previously reported for $[\text{TcOCl}(\text{SPhsal})]$ [13]. The rhenium atom is situated 0.692 Å above the basal plane of the oxygen, nitrogen, sulfur, and bromine atoms. This distance is within the range of 0.65–0.80 Å reported for comparable five-coordinate Tc(V) complexes [33]. However, this 0.692 Å displacement is smaller than that observed for most of the other five-coordinate species (0.70–0.85 Å) [34] due to the steric requirements of the π structure of the *O,N,S*-tridentate Schiff-base ligand [16]. The $\text{Re-S}_{\text{thiol}}$, $\text{Re-O}_{\text{alcohol}}$, Re-Br , and $\text{Re-N}_{\text{imine}}$ bond lengths are 2.27, 1.98, 2.47, and 2.09 Å, respectively.

The compounds $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{X-4-S})]$ ($\text{X}=\text{H}$ (**2**), Br (**3**), Cl (**4**), F (**5**), and OCH_3 (**6**)), as well as $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{X-4-CH}_2\text{S})]$ ($\text{X}=\text{H}$ (**7**), Cl (**8**), F (**9**), and OCH_3 (**10**)) are structurally identical with the exception of the *para*-substituent of the benzenethiol or benzylmercaptans. The structure of compound **2** is similar in nature to that of the Tc analog reported by Spies and co-workers in 1992 [15]. The core geometry of the five-coordinate oxorhenium–benzenethiol complexes is shown in Fig. 2 for $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_6\text{H}_4\text{F-4-S})]$ (**5**) and seen to consist of distorted square

pyramidal geometry. Similarly, the core geometry of the five-coordinate oxorhenium–benzylmercaptan complexes is shown in Fig. 3 for $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta\text{-C}_6\text{H}_4\text{F-4-CH}_2\text{S})]$ (**9**) and is also seen to consist of distorted square pyramidal geometry.

As shown in Fig. 4, the structure of $[\text{ReO}\{\eta^3\text{-(OC}_6\text{H}_4\text{C(H)NC}_6\text{H}_4\text{S)}\}(\eta^1\text{-C}_5\text{H}_4\text{NH-2-S})][\text{Br}]$ (**11**) consists of discrete complex cations and charge balancing Br^- anions. The rhenium coordination geometry is distorted square pyramidal, the prototypical geometry encountered for ‘3+1’ complexes with the $\{\text{MO}\}^{3+}$ core.

In all the oxorhenium benzenethiolates and benzylmercaptans, the basal plane is defined by an oxygen, nitrogen, and sulfur donor from the tridentate *O,N,S* Schiff-base, and an additional sulfur atom from the monodentate thiol, while an oxo group occupies the apical site. The distorted five-coordinate geometry may be quantified using the τ index described by Addison [35]. The measurement uses the two largest angles contained in the basal plane, which expressed in the form $(\beta-\alpha)/60$ give a unitless value ranging from 0 to 1, with a value of 0 for the square pyramidal limit and a value of 1 for the idealized trigonal bipyramid. The τ indices for the rhenium mixed thiolate compounds of this study are listed in Table 2, and are similar to those of other members of the oxorhenium ‘3+1’ mixed-thiolate family [26]. The nature of the ligands, specifically the steric requirements of the π structure of the Schiff-base ligand, the inability of the tridentate ligand to occupy the idealized equatorial positions while sterically blocking the sixth potential coordination position, as well as the strong *trans* influence of the terminal oxo group, constrain the complexes towards square pyramidal geometry.

In all cases, the apical position is occupied by a terminal oxo group with typical $\text{Re}=\text{O}$ distances ranging from approximately 1.67 to 1.69 Å. The four equatorial positions are occupied by an oxygen, nitrogen, and sulfurs donor of the tridentate *O,N,S* Schiff-base and the lone sulfur donor of the derivatized benzene-thiol and benzylmercaptan ligands. In the complexes of this study, the displacement of Re site from the equatorial plane in the direction of the oxo group is approximately 0.666–0.692 Å as shown in Table 3. The sulfur distances are all fairly unexceptional ranging from 2.26 to 2.33 Å, well within the range of those previously reported [36–38]. Also, the $\text{Re}-\text{O}_{\text{alcohol}}$ distances range from 1.96 to 1.99 Å, while the $\text{Re}-\text{N}_{\text{imine}}$ distances range from 2.08 to 2.12 Å. Table 3 compares the relative bond lengths for compounds **1**, **3**, **5–9**, and **11**.

4. Conclusion

Exploitation of the thiolate chemistry of the oxorhenium(V) core has allowed the preparation of a series of mononuclear, neutral oxorhenium-mixed thiolate complexes. The method of synthesis uses the ‘3+1’ technology for preparing oxorhenium(V)–thiolate complexes by direct one-pot reaction of $[\text{n-(C}_4\text{H}_9)_4\text{N}][\text{ReOBr}_4\text{-(OPPh}_3)]$ with the Schiff-base tridentate and monodentate ligands. This route appears to be a quite general, facile method for high yield synthesis of materials with the MO(V) core for $\text{M}=\text{Tc}$ and Re .

5. Supplementary material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. A view of the structure of [ReOBr{η³-(OC₆H₄C(H)NC₆H₄S)}] (1), showing the atom-labeling scheme and 50% thermal ellipsoids.

Fig. 2.

A view of the structure of [ReO{η³-(OC₆H₄C(H)NC₆H₄S)} (η¹-C₆H₄F-4-S)] (**5**), showing the atom-labeling scheme and 50% thermal ellipsoids.

Fig. 3.
A view of the structure of [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)} (η^1 -C₆H₄F-4-CH₂S)] (**9**), showing the atom-labeling scheme and 50% thermal ellipsoids.

Fig. 4. A view of the structure of [ReO{η³-(OC₆H₄C(H)NC₆H₄S)} (η¹-C₅H₄NH-2-S)][Br] (**11**), showing the atom-labeling scheme and 50% thermal ellipsoids.

Table 1

Summary of the crystallographic data for the compounds [ReOBr{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (1), [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (η^1 -C₆H₄Br-4-S)] (3), [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (η^1 -C₆H₄F-4-S)] (5), [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (η^1 -C₆H₄OCH₃-4-S)] (6), [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (η^1 -C₆H₅-4-CH₂S)] (7), [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (η^1 -C₆H₄Cl-4-CH₂S)] (8), [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (η^1 -C₆H₄F-4-CH₂S)] (9), [ReO{ η^3 -(OC₆H₄C(H)NC₆H₄S)}] (η^1 -C₅H₄NH-2-S)] [Br] (11)

	1	3	5	6	7	8	9	11
Chemical formula	C ₁₃ H ₉ NO ₂ SBrRe	C ₁₉ H ₁₃ NO ₂ S ₂ BrRe	C ₁₉ H ₁₃ NO ₂ S ₂ FRe	C ₂₀ H ₁₆ NO ₂ S ₂ Re	C ₂₀ H ₁₆ NO ₂ S ₂ Re	C ₂₀ H ₁₅ NO ₂ S ₂ CiRe	C ₂₀ H ₁₅ NO ₂ S ₂ FRe	C ₁₉ H ₁₆ N ₂ O ₂ S ₂ BrCl ₂ Re
<i>a</i> (Å)	8.9604(17)	15.707(5)	10.3384(15)	15.495(4)	13.189(3)	15.568(7)	7.699(2)	8.8021(12)
<i>b</i> (Å)	10.372(2)	9.990(3)	15.041(2)	9.834(2)	10.681(2)	10.237(4)	8.693(2)	11.2409(16)
<i>c</i> (Å)	14.427(3)	12.274(4)	22.802(4)	12.683(4)	13.683(3)	12.896(5)	13.969(4)	12.0597(17)
α (°)	90	90	90	90	90	90	82.650(5)	86.377(4)
β (°)	98.931(4)	103.109(5)	90	105.983(4)	103.296(4)	111.254(7)	82.729(9)	75.513(4)
γ (°)	90	90	90	90	90	90	77.068(5)	74.976(3)
<i>V</i> (Å ³)	1324.5(5)	1875.7(11)	3545.6(9)	1858.0(9)	1875.7(7)	1915.5(14)	899.0(4)	1115.8(3)
<i>Z</i>	4	4	8	4	4	4	2	2
FW	509.38	617.53	556.62	568.66	552.66	587.10	570.65	705.47
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> <i>bca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1
<i>T</i> (K)	94(5)	87(5)	90(5)	89(5)	91(5)	87(5)	85(5)	86(5)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>D</i> _{calc} (g cm ⁻³)	2.554	2.187	2.086	2.033	1.957	2.036	2.108	2.100
μ (mm ⁻¹)	12.343	8.845	7.113	6.786	6.715	6.717	7.016	7.681
<i>R</i> ^{<i>a</i>}	0.0498	0.0614	0.0357	0.0724	0.0432	0.0253	0.0750	0.0356
<i>wR</i> ₂ ^{<i>b</i>}	0.0980	0.1160	0.0527	0.1060	0.0994	0.0504	0.1352	0.097

^{*a*} $\Sigma|F_o| - |F_o|/\Sigma|F_o|$.

$$bwR_2 = \left[\frac{\Sigma \left[w(F_o^2 - F_c^2)^2 \right]}{\Sigma \left[w(F_o^2) \right]} \right]^{1/2}$$

Table 2

The τ index for the five-coordinate rhenium complexes of this study, as a measure of geometric distortion from idealized geometries

Compound	α^a	β^b	τ^c
[ReOBr(O–N–S)] (1)	134.2	151.2	0.28
[ReO(O–N–S)(η^1 -C ₆ H ₄ Br-4-S)] (3)	133.5	152.3	0.31
[ReO(O–N–S)(η^1 -C ₆ H ₄ F-4-S)] (5)	134.3	150.4	0.27
[ReO(O–N–S)(η^1 -C ₆ H ₄ OCH ₃ -4-S)] (6)	133.8	152.1	0.30
[ReO(O–N–S)(η^1 -C ₆ H ₅ -4-CH ₂ S)] (7)	137.3	147.4	0.17
[ReO(O–N–S)(η^1 -C ₆ H ₄ Cl-4-CH ₂ S)] (8)	140.1	145.9	0.10
[ReO(O–N–S)(η^1 -C ₆ H ₄ F-4-CH ₂ S)] (9)	135.7	151.4	0.26
[ReO(O–N–S)(η^1 -C ₅ H ₄ NH-2-S)][Br] (11)	138.0	147.2	0.15

^a α ≡the second largest basal angle.

^b β ≡the largest basal angle.

^c τ ≡($\beta - \alpha$)/60, O–N–S = η^3 -(OC₆H₄C(H)NC₆H₄S).

Table 3

Comparison of selected bond lengths ^a for rhenium-mixed thiolate complexes

Complex	Re=O	η^1 -thiolate		η^3 -donor (S1-N1-O2)			Δ Re ^b
		Re-S2	Re-S1	Re-N1	Re-O2		
1	1.673(6)	N/A	2.2671(19)	2.087(6)	1.978(5)	0.692	
3	1.683(5)	2.3103(19)	2.2628(18)	2.097(6)	1.970(5)	0.678	
5	1.688(3)	2.3020(14)	2.2697(13)	2.110(4)	1.990(3)	0.692	
6	1.690(5)	2.315(2)	2.271(2)	2.110(6)	1.988(5)	0.680	
7	1.692(4)	2.2871(15)	2.2790(15)	2.092(5)	1.979(4)	0.691	
8	1.681(2)	2.2891(10)	2.2820(10)	2.104(3)	1.983(2)	0.682	
9	1.671(6)	2.291(3)	2.263(2)	2.115(8)	1.962(7)	0.666	
11	1.685(4)	2.3267(12)	2.2691(11)	2.098(4)	1.987(3)	0.690	

^a Distances reported in Å with e.s.d.s in parentheses.

^b Δ Re: distance of the Re from the least squares plane of the equatorial donors.