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Synthesis and characterization of oxorhenium(V)–'3 + 1' mixed thiolate [SNS]/[S] and [ONS]/[S] complexes. Crystal and molecular structures of [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Br-4-S)], [ReO(η^3-$SCH_2C_5H_3NCH_2O$)(η^1-C_6H_4X-4-S)] (X = Cl, OMe), [ReO(η^3-$SCH_2C_5H_3NCH_2O$)(η^1-$C_6H_4OCH_3$-4-CH_2S)] and [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_5H_4NH-2-S)][Cl]

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Abstract

The reaction of [$ReOCl_3(PPh_3)_2$] with the tridentate ligands 2,6-dithiomethylpyridine (**4**) or 6-thiomethyl-2-pyridinemethanol (**5**) and the appropriate monothiols, such as *para*-substituted benzenethiols (C_6H_4X-4-SH) (where X = F, Cl, Br and OCH_3) and *para*-substituted benzylmercaptans (C_6H_4X-4-CH_2SH) (where X = F, Cl and OCH_3) in the presence of Et_3N leads to the isolation of a series of integrated '3 + 1' oxorhenium(V) complexes. Similarly, reaction of [$ReOCl_3(PPh_3)_2$] with 2-mercaptopyridine and **4** afforded a cationic oxorhenium(V) complex, [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_5H_4NH-2-S)][Cl] (**22**). Crystal data for **10**, $C_{13}H_{11}BrNOS_3Re$: triclinic, $P1$, $a = 7.2909(5)$, $b = 14.1978(9)$, $c = 15.991(1)$ Å, $\alpha = 77.184(1)$, $\beta = 86.588(1)$, $\gamma = 75.507(1)°$, $V = 1562.69(18)$ Å^3, $Z = 4$. For **16**, $C_{13}H_{11}ClNO_2S_2Re$: orthorhombic, $P2_12_12_1$, $a = 6.9728(6)$, $b = 13.477(1)$, $c = 15.761(1)$ Å, $V = 1481.1(2)$ Å^3, $Z = 4$. For **18**, $C_{14}H_{14}NO_3S_2Re$: monoclinic, $P2_1/c$, $a = 15.6512(14)$, $b = 7.6678(7)$, $c = 13.732(1)$ Å, $\beta = 112.489(1)°$, $V = 1522.7(2)$ Å^3, $Z = 4$. For **21**, $C_{15}H_{16}NO_3S_2Re$: monoclinic, $P2_1/c$, $a = 13.929(1)$, $b = 7.741(1)$, $c = 15.583(2)$ Å, $\beta = 103.600(2)°$, $V = 1633.1(3)$ Å^3, $Z = 4$. For **22**, $C_{12}H_{11}ClN_2OS_3Re$: monoclinic, $C2_1/c$, $a = 27.827(3)$, $b = 8.529(1)$, $c = 14.957(2)$ Å, $\beta = 119.314(2)°$, $V = 3095.3(6)$ Å^3, $Z = 8$.

Keywords: Crystal structures; Oxorhenium complexes; Mixed thiolate complexes

1. Introduction

Technetium-99m has become the isotope of choice in the development of diagnostic radioisotopes by virtue of its optimal nuclear properties (γ-emitter, $E_{max} = 140$ keV, $t_{1/2} = 6$ h) and the advantage of radionuclide availability through the molybdenum-99/technetium-99m generator system [1]. Furthermore, the radionuclides of rhenium, the group 7 congener of Tc, are β-emitters with properties which make them suitable for radiotherapeutic applications (^{186}Re: $E_{max} = 1.07$ MeV, $t_{1/2} = 90$ h; ^{188}Re: $E_{max} = 2.12$ MeV, $t_{1/2} = 17$ h) [2]. Chemists have been actively involved in technetium and rhenium coordination chemistry during the past few decades to design materials as potential radiopharmaceuticals. Continuous efforts are still applied to find efficient chelating systems for the $[MO]^{3+}$ cores (M = Tc and Re). A major class of technetium and rhenium complexes involves a tetradentate N_2S_2 donor system to the oxometal(V) core [3]. A considerable variety of such complexes has been prepared, evaluated, modified, and optimized in the attempt to achieve appropriate chemical stability, biomedical properties, and in vivo distribution behavior for specific imaging and therapy purposes. More recently the so-called '3 + 1' design, in

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which a neutral oxometal complex was prepared by employing the mixed tridentate and monodentate ligands with the appropriate MO(V) precursors. The advantage of such a '3 + 1' concept over N_2S_2 systems lies in the fact that '3 + 1' complexes lack *syn* and *anti* stereoisomers that are often produced in the tetradentate oxorhenium and technetium complexes. In addition, substituent modifications can be introduced at either the tridentate or monodentate ligand or at both sites with ease, whereas the attachment of a bifunctional linker onto a planar tetradentate ligand usually requires tremendous amount of synthetic effort [4].

Several examples of '3 + 1' ^{99m}Tc-oxo complexes incorporating biologically active fragments, such as tropane or ketanserin mimetics, have been proposed as receptor-binding tracers. All of these '3 + 1' complexes contain a dianionic tridentate ligand of the type [SXS], where X = S, O, or N(R) and a monodentate thiol, which usually bears a pharmacophore [5]. The major problem accompanied with these '3 + 1' systems was the relatively poor in vitro and in vivo stability of these complexes in whole blood due to metabolism and replacement of the monothiol group through transchelation by glutathione [6]. The rate of this metabolism is strongly dependent upon fine-tuning of structural variation of tridentate/monodentate ligands, especially of the tridentate ligand. For example, [SN(CH_3)S] donor complexes are significantly more stable than SSS complexes. To better understand the synergistic effects of '3 + 1' type of oxometal complexes, significant efforts to develop new tridentate ligands must be undertaken. Up to now, very little has been done on the [ONS] donor class of tridentate ligands due to the difficulty of synthesis. We recently reported a series of [ONS]/[S] '3 + 1' ReO(V) complexes, exploiting the tridentate Schiff-base [HOC_6H_4-2-C(H) = N–C_6H_4-2-SH] ligand which afforded phenol oxygen, imine nitrogen and benzene thiol as ONS donors. *para*-Substituted benzenethiols or benzylmercaptans were used as the monothiol donors [7]. As part of our continuing development of the coordination chemistry of Tc(V) and Re(V) complexes in order to provide new methodology for radiolabeling of chemotatic peptides, we now report herein on the synthesis and characterization of a series of [XNS]/[S] '3 + 1' complexes (where X = O or S). The [SNS] tridentate ligand used in this study is 2,6-dithiomethylpyridine (**4**) and the [ONS] tridentate ligand is 6-thiomethyl-2-pyridinemethanol (**5**).

2. Experimental

2.1. General considerations

NMR spectra were recorded on a Bruker DPX 300 (^{1}H 300.10 MHz) spectrometer in $CDCl_3$ (δ 7.27 ppm). IR spectra were recorded as KBr pellets with a Perkin–Elmer Series 1600 FTIR. Elemental analysis for carbon, hydrogen and nitrogen were carried out by Oneida Research Services, Whitesboro, NY. Analytical thin-layer chromatography (TLC) was performed with Merck silica gel F-254 glass-backed plates. Visualization was achieved by UV illumination. Flash chromatography was performed according to Still [8] using Aldrich silica gel (70–230 mesh). Ammonium perrhenate (Aldrich), 4-fluorobenzyl mercaptan (Lancaster), 4-chlorobenzyl mercaptan (Aldrich), 4-methoxybenzyl mercaptan (Lancaster), benzenethiol (Aldrich), 4-fluorobenzenethiol (Aldrich), 4-chlorobenzenethiol (Aldrich), 4-bromobenzenethiol (Aldrich), 4-methoxybenzenethiol (Aldrich), and 2,6-pyridinedimethanol (Aldrich) were used as received without further purification. $ReOCl_3(PPh_3)_2$ was prepared according to literature [9].

2.2. Synthesis

2.2.1. Preparation of 2,6-dibromomethylpyridine (2) and 2-bromomethyl-6-pyridinemethanol (3)

2,6-Dibromomethylpyridine (**2**) and 2-bromomethyl-6-pyridinemethanol (**3**) were prepared according to literature with modifications [10,11]. 2,6-Pyridinedimethanol (5 g, 36 mmol) in 48% aqueous HBr (60 cm^3) was heated under gentle reflux for 10 h. The completeness of the reaction was monitored by ^{1}H NMR by the disappearance of starting material. The resulting solution was cooled to 0°C, and neutralized by addition of aqueous sodium hydroxide (10 M, 60 cm^3). The temperature was kept below 5°C during the neutralization. The neutralized mixture was then diluted to 200 cm^3, and extracted with CH_2Cl_2 (3 × 100 cm^3). The combined extracts were collected, washed with a saturated aqueous NaCl and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a pink solid residue which was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to give 3.72 g of **2** (39%, m.p. 88–89°C) and 3.78 g of **3** (52%, m.p. 76–78°C). ^{1}H NMR ($CDCl_3$, ppm) for **2**: 4.54 (s, 4H, CH_2Br), 7.37 (d, J = 7.8 Hz, 2H, pyrH *meta*), 7.71 (t, J = 7.8 Hz, 1H, pyrH *para*). ^{1}H NMR ($CDCl_3$, ppm) for **3**: 3.70 (t, J = 5.6 Hz, 1H, OH), 4.55 (s, 2H, CH_2Br), 4.77 (d, J = 5.6 Hz, 2H, CH_2OH), 7.17 (d, J = 8.1 Hz, 1H, pyrH *ortho* to CH_2OH), 7.35 (d, J = 8.1 Hz, 1H, pyrH *ortho* to CH_2Br), 7.70 (t, J = 8.1 Hz, 1H, pyrH *para*). *Caution!!* Dibromide **2** and monobromide **3** are strong lachrymators and trace amount of each may be dermatic.

2.2.2. Preparation of tridentate ligands 2,6-dithiomethylpyridine (4) and 6-thiomethyl-2-pyridinemethanol (5)

2.2.2.1. Preparation of 2,6-dithiomethylpyridine (4). 2,6-Dithiomethylpyridine (**4**) was prepared according to the

method of Constable et al. [12] with minor modifications. After decomposition of 2,6-bis[(methylthiocarbamoylthio)methyl]pyridine using NaOH, the reaction mixture was cooled to room temperature and neutralized to pH 5 with concentrated hydrochloric acid and extracted with chloroform (3×100 cm^3). The combined extracts were washed with H_2O, and concentrated NaCl solution and dried over $MgSO_4$. The solvent was removed under reduced pressure to give **4** as yellow oil. Further column chromatographic purification was made on silica gel using $CHCl_3$ as the eluent under a nitrogen atmosphere. The colorless syrup was stored under nitrogen and solidified upon standing. Yield: 55%. B.p. 96–102°C/0.2 mmHg. ^{1}H NMR ($CDCl_3$, ppm): 2.02 (t, $J = 7.9$ Hz, 2H, –SH), 3.82 (d, $J = 7.9$ Hz, 4H, CH_2SH), 7.21 (d, $J = 7.8$ Hz, 2H, pyrH *meta*), 7.62 (t, $J = 7.8$ Hz, 1H, pyrH *para*). *Anal.* Calc. for $C_7H_9NS_2$: C, 49.1; H, 5.26; N, 8.19. Found: C, 49.3; H, 5.10; N, 8.30%.

*2.2.2.2. Preparation of 6-thiomethyl-2-pyridinemethanol (**5**).* Although compound **5** has been reported in a patent by one-pot reaction from 2,6-pyridinedimethanol, thiourea and 48% HBr [13], we were unable to repeat the reaction. Instead we developed the following procedure: 2-bromomethyl-6-pydinemethanol (**3**) (3 g, 14.9 mmol) and thiourea (1.18 g, 15.5 mmol) were dissolved in EtOH (30 cm^3) and the mixture was heated to reflux for 8 h, after which the solution was evaporated to dryness under reduced pressure to give a pale yellow oil. The thiouronium salt 6-[(methylthiocarbamoylthio)methyl]-2-pyridinemethanol was then treated with a solution of NaOH (1 g, 25 mmol) in H_2O (20 cm^3) to give a clear solution. The solution was then heated under reflux for 2 h in a stream of nitrogen. The reaction mixture was then cooled to room temperature and neutralized to pH 5 with concentrated HCl and extracted with $CHCl_3$ (3×100 cm^3). The combined extracts were washed with H_2O, concentrated NaCl solution, and the solvent removed in vacuo to give a pale yellow oil which solidified upon standing in refrigerator overnight. Yield: 1.11 g (48%). M.p. 63–66°C (dec.) ^{1}H NMR ($CDCl_3$, ppm): 3.85 (d, $J = 3$Hz, 2H, CH_2SH), 4.74 (s, 2H, CH_2OH), 7.12 (d, $J = 7.8$ Hz, 1H, pyrH *ortho* to CH_2SH), 7.26 (d, $J = 7.8$ Hz, 1H, pyrH *ortho* to CH_2OH), 7.67 (t, $J = 7.8$ Hz, 1H, pyrH *para*). *Anal.* Calc. for C_7H_9NOS: C, 54.2; H, 5.81; N, 9.03. Found: C, 54.4; H, 5.95; N, 9.08%.

*2.2.3. General procedure for the preparation of [ReOCl(η^3-$XCH_2C_5H_3NCH_2S$)(PPh_3)] where X = S (**6**), and X = O (**7**)*

To a stirred suspension of trichlorobis(triphenylphosphine)rhenium(V) oxide (83 mg, 0.1 mmol) in chloroform (30 cm^3) was added 2,6-dithiomethylpyridine (**4**) or 6-thiomethyl-2-pyridinemethanol (**5**) in $CHCl_3$ (0.1 M, 1 cm^3) and the mixture was refluxed until the green–yellow color of the precursor turned to grass-green. After being cooled to room temperature, the reaction mixture was washed with water. The organic layer was separated from the mixture and dried over Na_2SO_4. The volume was reduced to 3 cm^3 and then purified on silica gel column using gradient eluent (from 100% $CHCl_3$ to 100% acetone).

*2.2.3.1. [ReOCl(η^3-$SCH_2C_5H_3NCH_2S$)(PPh_3)] (**6**).* (Yield: 50 mg, 75%). FTIR (cm^{-1}, KBr pellet): 968 (Re=O). *Anal.* Calc. for $C_{25}H_{22}ClNOS_2PRe$: C, 44.9; H, 3.29; N, 2.09. Found: C, 44.5; H, 3.41; N, 2.02%.

*2.2.3.2. [ReOCl(η^3-$OCH_2C_5H_3NCH_2S$)(PPh_3)] (**7**).* (Yield: 41 mg, 63%). FTIR (cm^{-1}, KBr pellet): 970 (Re=O). *Anal.* Calc. for $C_{25}H_{22}ClNO_2SPRe$: C, 46.0; H, 3.37; N, 2.15. Found: C, 45.8; H, 3.29; N, 2.30%.

*2.2.4. General procedure for the preparation of [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4X-4-S)] where X = F(**8**), Cl(**9**), Br(**10**), and OCH_3 (**11**)*

To a stirred suspension of trichlorobis(triphenylphosphine)rhenium(V) oxide (83 mg, 0.1 mmol) in $CHCl_3$ (30 cm^3) was added dropwise with stirring a $CHCl_3$ solution (5 cm^3) consisting of one equivalent of 2,6-dithiomethylpyridine (**4**) (1 M, 1 cm^3) and one equivalent of the benzenethiol [C_6H_4X-4-S] (X = F, Cl, Br, and OCH_3) (0.1 mmol). A reddish brown solution formed immediately, which intensified when Et_3N (2 drops) was added. The reaction was stirred under reflux for 20 min, concentrated and purified by flash chromatography. The eluent first applied was $CHCl_3$ to remove PPh_3 and trace amounts of unreacted thiols; then 10% acetone–$CHCl_3$ was used to obtain the product as a reddish solid. X-ray quality crystals for compound **10** were grown by slow diffusion of ethyl ether into a solution of the compound dissolved in minimum amount of CH_2Cl_2.

*2.2.4.1. [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4F-4-S)] (**8**).* (Yield: 31 mg, 62%). FTIR (cm^{-1}, KBr pellet): 963 (Re=O). ^{1}H NMR ($CDCl_3$, ppm): 4.97 (d, $J = 18$ Hz, 2H, $-SCH_2$), 5.2 (s br, 1H, $-SCH_2$), 5.5 (s br, 1H, $-SCH_2$), 7.10 (dd, $J = 8.7$ Hz, 2H, –SArH), 7.6–7.7 (dd, $J = 7.8$ Hz, 2H, pyrH *meta*), 7.8 (d, $J = 7.8$ Hz, 1H, pyrH *para*), 8.00 (dd, $J = 8.7$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{13}H_{11}NOFS_3Re$: C, 31.3; H, 2.21; N, 2.81. Found: C, 31.6; H, 2.18; N, 2.79%.

*2.2.4.2. [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Cl-4-S)] (**9**).* (Yield: 28 mg, 54%). FTIR (cm^{-1}, KBr pellet): 965 (Re=O). ^{1}H NMR ($CDCl_3$, ppm): 4.98 (d, $J = 16$ Hz,

2H, $-SCH_2$), 5.1–5.6 (m, 2H, $-SCH_2$), 7.35 (d, $J = 8.4$ Hz, 2H, –SArH), 7.61 (d, $J = 8.7$ Hz, 2H, pyrH *meta*), 7.81 (d, $J = 8.7$ Hz, 1H, pyrH *para*), 8.00 (dd, $J = 8.4$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{13}H_{11}NOClS_3Re$: C, 30.3; H, 2.14; N, 2.72. Found: C, 30.6; H, 2.23; N, 2.88%.

*2.2.4.3. [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Br-4-S)] (**10**).* (Yield: 37 mg, 67%). FTIR (cm^{-1}, KBr pellet): 965 (Re=O). ^1H NMR ($CDCl_3$, ppm): 4.97 (d, $J = 16$ Hz, 2H, $-SCH_2$), 5.1–5.6 (m, 2H, $-SCH_2$), 7.45–7.60 (m, 4H, 2-SArH and 2 pyrH *meta*), 7.83 (d, $J = 8.7$ Hz, 1H, pyrH *para*), 7.99 (dd, $J = 7.8$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{13}H_{11}NOBrS_3Re$: C, 27.9; H, 1.97; N, 2.50. Found: C, 28.0; H, 2.04; N, 2.39%.

*2.2.4.4. [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-$C_6H_4OCH_3$-4-S)] (**11**).* (Yield: 33 mg, 65%). FTIR (cm^{-1}, KBr pellet): 968 (Re=O). ^1H NMR ($CDCl_3$, ppm): 3.85 (s, 3H, OCH_3), 4.98 (d, $J = 15$ Hz, 2H, $-SCH_2$), 5.2 (s br, 1H, $-SCH_2$), 5.55 (s br, 1H, $-SCH_2$), 6.96 (d, $J = 8.7$ Hz, 2H, –SArH), 7.59 (d, $J = 8.7$ Hz, 2H pyrH *meta*), 7.8 (m, 1H, pyrH *para*), 8.00 (dd, $J = 8.7$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{14}H_{14}NO_2S_3Re$: C, 32.9; H, 2.75; N, 2.75. Found: C, 32.8; H, 2.83; N, 2.71%.

*2.2.5. General procedure for the preparation of [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4X-4-CH_2S)] where X = F(**12**), Cl(**13**), and OCH_3 (**14**)*

To a refluxing solution of [ReOCl(η^3-$SCH_2C_5H_3NCH_2S$)(PPh_3)] (**6**) (33.5 mg, 0.05 mmol) in acetonitrile (10 cm^3) was added dropwise a solution of benzenethiol [C_6H_4X-4-CH_2S] (X = F, Cl, and OCH_3) (0.1 mmol) in acetonitrile (3 cm^3). The solution turned from grass-green to wine-red color. Upon addition of three drops of Et_3N, the color of the reaction mixture turned immediately from red to brown. The solution was stirred and refluxed for an additional 15 min and was then evaporated to dryness. The dark red residue was purified by a short silica gel column similar to that mentioned above.

*2.2.5.1. [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4F-4-CH_2S)] (**12**).* (Yield: 29 mg, 56%). FTIR (cm^{-1}, KBr pellet): 967 (Re=O). ^1H NMR ($CDCl_3$, ppm): 4.9–5.0 (m, 2H, $-SCH_2$), 5.02 (d, $J = 16$ Hz, 2H, $-SCH_2$), 5.47 (d, $J = 16$ Hz, 2H, $-SCH_2$), 7.00 (dd, $J = 8.7$ Hz, 2H, –SArH), 7.69–7.74 (dd, $J = 5.6$ Hz, 2H, pyrH *meta*), 7.83 (d, $J = 7.8$ Hz, 1H, pyrH *para*), 8.00 (dd, $J = 7.6$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{14}H_{13}NOFS_3Re$: C, 32.8; H, 2.54; N, 2.73. Found: C, 33.0; H, 2.48; N, 2.83%.

*2.2.5.2. [ReO(η^3–$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Cl-4-CH_2S)] (**13**).* (Yield: 35 mg, 66%). FTIR (cm^{-1}, KBr pellet): 960 (Re=O). ^1H NMR ($CDCl_3$, ppm): 5.01 (d, $J = 15$ Hz, 2H, $-SCH_2$), 5.48 (d, $J = 15$ Hz, 2H, $-SCH_2$), 7.32 (dd, $J = 8.7$ Hz, 2H, –SArH), 7.61 (dd, $J = 7.8$ Hz, 2H, pyrH *meta*), 7.82 (d, $J = 7.8$ Hz, 1H, pyrH *para*), 8.05 (dd, $J = 7.6$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{14}H_{13}NOClS_3Re$: C, 31.8; H, 2.46; N, 2.65. Found: C, 32.0; H, 2.37; N, 2.73%.

*2.2.5.3. [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-$C_6H_4OCH_3$-4-CH_2S)] (**14**).* (Yield: 28 mg, 53%). FTIR (cm^{-1}, KBr pellet): 965 (Re=O). ^1H NMR ($CDCl_3$, ppm): 3.79 (s, 3H, $-OCH_3$), 4.9–5.0 (m, 2H, $-SCH_2$), 5.03 (d, $J = 15$ Hz, 2H, $-SCH_2$), 5.50 (d, $J = 15$ Hz, 2H, $-SCH_2$), 6.85 (d, $J = 7.8$ Hz, 2H, –SArH), 7.35 (d, $J = 8.7$ Hz, 2H, pyrH *meta*), 7.62 (d, $J = 8.7$ Hz, 1H, pyrH *para*), 8.00 (dd, $J = 7.8$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{15}H_{16}NO_2S_3Re$: C, 34.4; H, 3.05; N, 2.67. Found: C, 34.2; H, 2.98; N, 2.81%.

*2.2.6. General procedure for the preparation of [ReO(η^3-$SCH_2C_5H_3NCH_2O$)(η^1-C_6H_4X-4-S)] where X = F(**15**), Cl(**16**), Br(**17**), and OCH_3 (**18**)*

To a stirred suspension of trichlorobis(triphenylphosphine)rhenium(V) oxide (83 mg, 0.1 mmol) in $CHCl_3$ (30 cm^3) was added dropwise with stirring a $CHCl_3$ solution (5 cm^3) consisting of one equivalent of 6-thiomethyl-2-pyridinemethanol (**5**) in $CHCl_3$ (0.1 M, 1 cm^3) and one equivalent of the benzenethiol [C_6H_4X-4-S] (X = F, Cl, Br, and OCH_3) (0.1 mmol). Et_3N (4 drops) was then added and the resulting solution was refluxed for 20 min until the green–yellow color of the precursor turned to reddish-brown. The dark red product was purified as mentioned above for the [SNS]/[S] analogs. X-ray quality crystals for compounds **16** and **18** were grown by slow diffusion of pentane into a solution of the compounds dissolved in CH_2Cl_2.

*2.2.6.1. [ReO(η^3-$OCH_2C_5H_3NCH_2S$)(η^1-C_6H_4F-4-S)] (**15**).* (Yield: 27 mg, 57%). FTIR (cm^{-1}, KBr pellet): 958 (Re=O). ^1H NMR ($CDCl_3$, ppm): 4.78 (d, $J = 16$ Hz, 1H, $-SCH_2$), 5.34 (s br, 1H, $-OCH_2$), 6.0–6.2 (m, 2H, $-SCH_2$ and $-OCH_2$), 6.98 (d, $J = 7.8$ Hz, 2H, –SArH), 7.63 (d, $J = 8.7$ Hz, 2H, pyrH *meta*), 7.81 (d, $J = 8.7$ Hz, 1H, pyrH *para*), 8.01 (dd, $J = 7.8$ Hz, 2H, –SArH). *Anal.* Calc. for $C_{13}H_{11}NO_2FS_2Re$: C, 32.4; H, 2.28; N, 2.90. Found: C, 32.5; H, 2.19; N, 3.01%.

*2.2.6.2. [ReO(η^3-$OCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Cl-4-S)] (**16**).* (Yield: 31 mg, 64%). FTIR (cm^{-1}, KBr pellet): 962 (Re=O). ^1H NMR ($CDCl_3$, ppm): 4.78 (d, $J = 16$ Hz, 1H, $-SCH_2$), 5.40 (s br, 1H, $-OCH_2$), 6.0–6.2 (m, 2H, $-SCH_2$ and $-OCH_2$), 7.31 (d, $J = 7.8$ Hz, 2H, –SArH), 7.58 (d, $J = 8.7$ Hz, 2H, pyrH *meta*), 7.84 (d, $J = 8.7$ Hz, 1H, pyrH *para*), 8.02 (dd, $J = 7.8$ Hz, 2H,

–SArH). *Anal*. Calc. for $C_{13}H_{11}NO_2ClS_2Re$: C, 31.3; H, 2.21; N, 2.81. Found: C, 31.1; H, 2.35; N, 2.77%.

*2.2.6.3. [ReO(η³-OCH₂C₅H₃NCH₂S)(η¹-C₆H₄Br-4-S)] (**17**).* (Yield: 37 mg, 69%). FTIR (cm^{-1}, KBr pellet): 956 (Re=O). ^1H NMR ($CDCl_3$, ppm): 4.81 (d, $J = 16$ Hz, 1H, $-SCH_2$) 5.45 (s br, 1H, $-OCH_2$), 6.0–6.2 (m, 2H, $-SCH_2$ and $-OCH_2$), 7.48 (d, $J = 7.8$ Hz, 2H, –SArH), 7.60 (d, $J = 8.7$ Hz, 2H, pyrH *meta*), 7.82 (d, $J = 8.7$ Hz, 1H, pyrH *para*), 8.00 (dd, $J = 7.8$ Hz, 2H, –SArH). *Anal*. Calc. for $C_{13}H_{11}NO_2BrS_2Re$: C, 28.7; H, 2.03; N, 2.58. Found: C, 28.6; H, 1.94; N, 2.51%.

*2.2.6.4. [ReO(η³–OCH₂C₅H₃NCH₂S)(η¹-C₆H₄OCH₃-4-S)] (**18**).* (Yield: 33 mg, 66%). FTIR (cm^{-1}, KBr pellet): 962 (Re=O). ^1H NMR ($CDCl_3$, ppm): 3.84 (s, 3H, $-OCH_3$), 4.76 (d, $J = 18$ Hz, 1H, $-SCH_2$), 5.35 (s br, 1H, $-OCH_2$), 6.10–6.25 (m, 2H, $-SCH_2$ and $-OCH_2$), 6.93 (d, $J = 8.7$ Hz, 2H, –SArH), 7.60 (d, $J = 8.4$ Hz, 2H, pyrH *meta*), 7.80 (dd, $J = 8.4$ Hz, 1H, pyrH *para*), 8.02 (dd, $J = 8.7$ Hz, 2H, –SArH). *Anal*. Calc. for $C_{14}H_{14}NO_3S_2Re$: C, 34.0; H, 2.83; N, 2.83. Found: C, 33.9; H, 2.93; N, 2.80%.

*2.2.7. General procedure for the preparation of [ReO(η³-OCH₂C₅H₃NCH₂S)(η¹- C₆H₄X-4-CH₂S)] where X = F(**19**), Cl(**20**), and OCH₃ (**21**)*

To a refluxing solution of [ReOCl(η³-$OCH_2C_5H_3NCH_2S$)] (**7**) (33 mg, 0.05 mmol) in acetonitrile (10 cm^3) was added dropwise a solution of benzylmercaptan [C_6H_4X-4-CH_2S] (X = F, Cl, and OCH_3) (0.1 mmol) in acetonitrile (3 cm^3). The solution turned from grass green to reddish. Upon addition of 6 drops of Et_3N, the color of the reaction mixture turned immediately from red to brown. The solution was stirred and refluxed for an additional 45 min and then evaporated to dryness. Column purification was similar to the procedure mentioned above. X-ray quality crystals for compound **21** were grown by slow diffusion of pentane in a solution of the compounds dissolved in CH_2Cl_2.

*2.2.7.1. [ReO(η³-OCH₂C₅H₃NCH₂S)(η¹-C₆H₄F-4-CH₂S)] (**19**).* (Yield: 31 mg, 57%). FTIR (cm^{-1}, KBr pellet): 960 (Re=O). ^1H NMR ($CDCl_3$, ppm): 4.79 (d, $J = 18$ Hz, 1H, $-SCH_2$), 5.0 (m, 2H, $-SCH_2$), 5.45 (s br, 1H, $-OCH_2$), 6.05–6.25 (m, 2H, $-SCH_2$ and $-OCH_2$), 7.09 (dd, $J = 8.7$ Hz, 2H, –SArH), 7.6–7.7 (dd, $J = 8.7$ Hz, 2H, pyrH *meta*), 7.82 (dd, $J = 8.7$ Hz, 1H, pyrH *para*), 8.06 (dd, $J = 7.8$ Hz, 2H, –SArH). *Anal*. Calc. for $C_{14}H_{13}NO_2ClS_2Re$: C, 33.9; H, 2.62; N, 2.82. Found: C, 34,0; H, 2.57; N, 2.95%.

*2.2.7.2. [ReO(η³-OCH₂C₅H₃NCH₂S)(η¹-C₆H₄Cl-4-CH₂S)] (**20**).* (Yield: 33 mg, 64%). FTIR (cm^{-1}, KBr pellet): 962 (Re=O). ^1H NMR ($CDCl_3$, ppm): 4.78 (d, $J = 18$ Hz, 1H, $-SCH_2$), 4.9–5.0 (m, 2H, $-SCH_2$), 5.5 (s br, 1H, $-OCH_2$), 6.0 (s br, 1H, $-SCH_2$), 6.2 (s br, 1H, $-OCH_2$), 7.34 (d, $J = 8.1$ Hz, 2H, –SArH), 7.6–7.7 (dd, $J = 8.1$ Hz, 2H, pyrH *meta*), 7.82 (d, $J = 8.1$ Hz, 1H, pyrH *para*), 8.05 (dd, $J = 7.8$ Hz, 2H, –SArH). *Anal*. Calc. for $C_{14}H_{13}NO_2ClS_2Re$: C, 32.8; H, 2.54; N, 2.73. Found: C, 32.6; H, 2.35; N, 2.91%.

*2.2.7.3. [ReO(η³-OCH₂C₅H₃NCH₂S)(η¹-C₆H₄OCH₃-4-CH₂S)] (**21**).* (Yield: 28 mg, 55%). FTIR (cm^{-1}, KBr pellet): 957 (Re=O). ^1H NMR ($CDCl_3$, ppm): 3.78 (s, 3H, $-OCH_3$), 4.78 (d, $J = 18$ Hz, 1H, $-SCH_2$), 4.9–5.0 (m, 2H, $-SCH_2$), 5.5 (m, 1H, $-OCH_2$), 6.12(d, $J = 18$ Hz, 1H, $-SCH_2$), 6.25 (s br, 1H, $-OCH_2$), 6.84 (d, $J = 8.4$ Hz, 2H, –SArH), 7.34 (d, $J = 7.8$ Hz, 2H, pyrH *meta*), 7.65, 7.81 (dd, $J = 7.8$ Hz, 1H, pyrH *para*), 8.03 (dd, $J = 7.8$ Hz, 2H, –SArH). *Anal*. Calc. for $C_{15}H_{16}NO_3S_2Re$: C, 35.4; H, 3.15; N, 2.76. Found: C, 35.7; H, 3.03; N, 2.85%.

*2.2.8. Preparation of [ReO(η³-SCH₂C₅H₃NCH₂S)(η¹-C₅H₄NH-2-S)][Cl] (**22**)*

To a solution of [ReOCl(η³-$SCH_2C_5H_3NCH_2S$)-(PPh_3)] (6) (20 mg, 0.03 mmol) in methanol (20 cm^3) was added 2-mercaptopyridine (11 mg, 0.1 mmol) and the resulting mixture was refluxed for 30 min, and subsequently evaporated to dryness. The pink residue was dissolved in methanol and layered with ethyl ether to form crystals of **22** suitable for X-ray crystallography. (Yield: 7 mg, 41%). *Anal*. Calc. for $C_{12}H_{12}ClN_2OS_3Re$: C, 27.8; H, 2.32; N, 5.41. Found: C, 28.0; H, 2.18; N, 5.35%.

2.3. X-ray crystallography

The selected crystals of **10**, **16**, **18**, **21** and **22** were measured with a Siemens P4 diffractometer equipped with the SMART CCD system [14] and using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data collections were carried out 89(5) K. The data were corrected for Lorentz and polarization effects, and absorption corrections were made using SADABS [15]. Neutral atom scattering factors were taken from Cromer and Waber [16]. And anomalous dispersion corrections were taken from those of Creagh and McAuley [17]. All calculations were performed using SHELXL [18]. The structures were solved by direct methods [19] and all of the non-hydrogen atoms were located from the initial solution. After locating all the initial nonhydrogen atoms in each structure, the models were refined against F^2, initially using isotropic and later anisotropic thermal displacement parameters until the final value of Δ/σ_{max} was less than 0.001. At this point the hydrogen atoms were located from the electron density difference map and a final cycle of refinements was performed, until the final value of Δ/σ_{max}

Table 1
Summary of crystal, intensity, collection, and refinement data for complexes [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Br-4-S)] (**10**), [ReO(η^3-$SCH_2C_5H_3NCH_2O$)(η^1-C_6H_4-Cl-4-S)] (**16**), [ReO(η^3-$SCH_2C_5H_3NCH_2O$)(η^1-C_6H_4-OCH_3-4-S)] (**18**), [ReO(η^3-$SCH_2C_5H_3NCH_2O$)(η^1-$C_6H_4OCH_3$-4-CH_2S)] (**21**) and [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_5H_4NH-2-S)][Cl] (**22**)

	10	**16**	**18**	**21**	**22**
Empirical formula	$C_{13}H_{11}BrNOS_3Re$	$C_{13}H_{11}ClNO_2S_2Re$	$C_{14}H_{14}NO_3S_2Re$	$C_{15}H_{16}NO_3S_2Re$	$C_{12}H_{11}ClN_2OS_3Re$
Formula weight	559.52	499.00	494.58	508.61	517.06
Crystal size (mm)	$0.1\times0.1\times0.05$	$0.5\times0.5\times0.3$	$0.2\times0.1\times0.04$	$0.5\times0.1\times0.04$	$0.15\times0.1\times0.1$
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$C2_1/c$
Unit cell dimensions					
a (Å)	7.2909(5)	6.9728(6)	15.651(1)	13.930(1)	27.827(3)
b (Å)	14.1978(9)	13.477(1)	7.6678(7)	7.741(1)	8.5287(10)
c (Å)	15.991(1)	15.761(1)	13.732(1)	15.583(2)	14.9574(18)
α (°)	77.184(1)	90	90	90	90
β (°)	86.588(1)	90	112.489(1)	103.600(2)	119.314(2)
γ (°)	75.507(1)	90	90	90	90
V (Å^3)	1562.7(2)	1481.1(2)	1522.7(2)	1633.1(3)	3095.3(6)
Z	4	4	4	4	8
D_{calc} (Mg m^{-1})	2.378	2.238	2.157	2.069	2.219
$F(000)$	1048	944	944	976	1960
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	10.726	8.665	8.262	7.706	8.423
θ Range (°)	1.31–28.33	1.99–28.3	2.82–28.29	1.50–28.3	1.68–28.27
h, k, l	−9/9; −18/14; −21/20	−9/8; −17/17; −20/17	−20/15; −10/0; −18/18	−18/18; −9/10; −15/20	−32/36; −8/11; −19/19
No. of reflections	10612	9872	9618	10178	9964
No. of unique data	7212	3554	3624	3804	3700
R_{int} (%)	3.70	3.85	4.30	11.29	3.64
Parameters refined	361	182	190	200	181
Final indices (2σ data), R_1 [a] (wR_2)	0.0414 (0.0927)	0.0312 (0.0761)	0.0473 (0.1168)	0.0658 (0.1746)	0.0256 (0.0579)
All data, R_1 [a] (wR_2)	0.0597 (0.0996)	0.0319 (0.0764)	0.0522 (0.1200)	0.0685 (0.1780)	0.0340 (0.0603)
Goodness-of-fit, S (F^2)	0.985	1.069	1.066	1.043	1.032

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

was again less than 0.001. No anomalies were encountered in the refinement of any of the structures. The relevant parameters for crystal data, data collection, structure solution and refinement are summarized in Table 1, and important bond lengths and angles in Table 2 and Table 3. A complete description of the details of the crystallographic methods is given in Section 5.

3. Results and discussion

3.1. Synthesis and general properties

As shown in Fig. 1, the tridentate [SNS] (**4**) and [ONS] (**5**) ligands can be synthesized from the dibromide (**2**) and monobromide (**3**) precursors through the thiouronium salts and subsequent decomposition under basic condition. The '3 + 1' complexes **8**–**22** can be prepared using either one-pot or a two-step synthesis. When the monothiolate ligand is a *para*-substituted benzenethiol, one-pot synthesis is more effective. However, when the monothiolate ligand is a *para*-substituted benzyl mercaptan, two-step synthesis gives higher yields of monophasic material than one-pot reaction. In the first step of a two-step strategy, the labile precursor $[ReOCl_3(PPh_3)_2]$ was reacted with equivalent amount of

Table 2
Selected bond distances (Å) and angles (°) for complexes **10** and **22**

	10	**22**
Re–S(1)	2.290(2)	2.291(1)
Re–S(2)	2.294(2)	2.292(1)
Re–S(3)	2.306(2)	2.317(1)
Re–N(1)	2.107(6)	2.105(3)
Re–O(1)	1.690(5)	1.688(3)
S(1)–Re–S(2)	136.79(7)	136.38(4)
S(1)–Re–S(3)	89.84(7)	90.29(4)
S(2)–Re–S(3)	83.16(7)	83.88(4)
S(1)–Re–N(1)	81.35(17)	81.18(9)
S(2)–Re–N(1)	81.00(17)	81.33(9)
S(3)–Re–N(1)	145.63(18)	147.81(9)
S(1)–Re–O(1)	111.84(19)	111.82(10)
S(2)–Re–O(1)	110.96(19)	111.31(10)
S(3)–Re–O(1)	107.26(17)	106.25(10)
N(1)–Re–O(1)	106.9(2)	105.74(13)

Table 3
Selected bond distances (Å) and angles (°) for complexes **16**, **18** and **21**

	16	18	21
Re–S(1)	2.268(2)	2.287(2)	2.289(2)
Re–S(2)	2.295(1)	2.285(2)	2.284(2)
Re–O(2)	1.987(4)	2.015(6)	2.042(5)
Re–N(1)	2.073(5)	2.063(7)	2.096(5)
Re–O(1)	1.675(5)	1.679(6)	1.693(5)
S(1)–Re–S(2)	92.70(6)	87.31(8)	87.84(7)
S(1)–Re–O(2)	136.49(13)	138.10(16)	136.16(14)
S(2)–Re–O(2)	82.39(14)	87.83(15)	88.56(13)
S(1)–Re–N(1)	80.69(16)	79.9(2)	78.91(16)
S(2)–Re–N(1)	141.10(14)	141.00(17)	142.88(7)
O(2)–Re–N(1)	76.93(19)	78.2(2)	78.1(2)
S(1)–Re–O(1)	109.96(17)	109.6(2)	109.60(19)
S(2)–Re–O(1)	107.90(16)	107.7(2)	106.31(18)
O(2)–Re–O(1)	112.7(2)	111.5(3)	113.3(2)
N(1)–Re–O(1)	110.4(2)	111.3(3)	110.8(2)

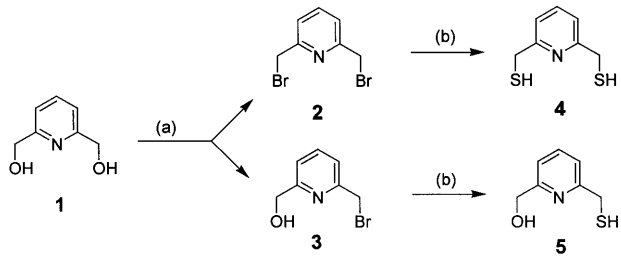

Fig. 1. Reaction scheme for the preparation of tridentate ligands **4** and **5**. (a) 48% HBr; (b) (1) thiourea, EtOH; (2) NaOH.

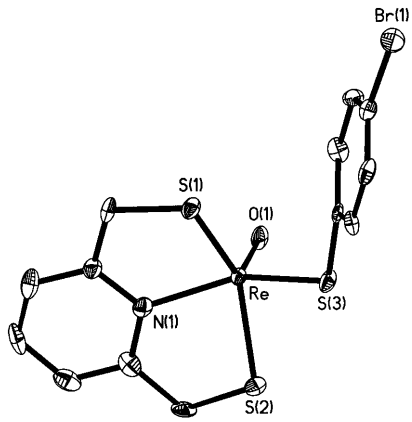

Fig. 2. ORTEP drawing of [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Br-4-S)] (**10**). Ellipsoids corresponds to 50% probability.

the tridentate ligand to give [ReOCl(η^3-$SCH_2C_5H_3NCH_2S$)(PPh_3)] (**6**) or [ReOCl(η^3-$OCH_2C_5H_3NCH_2S$)(PPh_3)] (**7**). The intermediate was then reacted with excess amount of *para*-substituted benzylmercaptans in refluxing chloroform with the existence of Et_3N until the original red color turned to dark brown. Purification of the raw material via column chromatography on silica gel yielded the neutral 5-coordinated 16-electron complexes [20].

Elemental analyses, as given in Section 2, were in good agreement with the proposed formulations. The IR spectra exhibit the characteristic Re=O stretching vibration around 960 cm^{-1} [21]. Due to the symmetry of the complexes **8**–**11** (vide infra), the corresponding protons of the two methylene thiolate arms resonated at the same frequency at room temperature. However, germinal protons at the same methylene carbon of the tridentate [SNS] backbone were distinguished as *endo* (protons pointing toward the oxygen) and *exo* (protons pointing away from the oxygen) [22,23]. Proton resonances of the methylene backbone and pyridine ring were all shifted downfield. The observed differences between *meta* and *para* protons of the pyridine ring decreased from 0.4 ppm in the uncomplexed form to 0.2 ppm in the oxorhenium complexes. The *para*-substituent on the aromatic ring of monothiolate ligands had little effect on the chemical shifts of protons of the chelated tridentate ligand backbone, since variation of the *para*-substituent from F (**8**) to Br (**10**) to OCH_3 (**11**) produced no significant changes in the chemical shifts of the ligand backbone atoms. This fact indicated that electronic properties of the ring were not transmitted to the chelated part of the ligand through the metal core of this type of complex. Changing the monothiol ligand from *para*-substituted benzenethiols to *para*-substituted benzyl mercaptans resulted, again, in little influence on the chemical shifts of the [SNS] ligand backbone. Because of the fast rotation of the benzyl methylene group, no distinction between the two protons on this carbon was observed at room temperature. A broadened singlet was thus seen overlapping with the *endo* protons of the methylene thiolate at around 5 ppm. Two doublets were observed for the *endo* and *exo* protons on the methylene thiolate backbone of the [ONS]/[S] '3 + 1' complexes. Despite the differences of the monothiolate ligands, chemical shifts for the protons assigned to *endo* position of the methylene thiolate of the [ONS] tridentate ligand was around 4.7 ppm, and the *exo* position at 6.1 ppm. Due to the more rapid rotational scrambling of the protons on the hydroxymethyl pyridine methylene carbon than the protons on the methylene thiolate backbone, no sharp AB doublet pattern was observable, but rather two broad coalesced singlets were seen at approximately 5.4 ppm for the *endo* proton and 6.3 ppm for the *exo* proton, respectively.

3.2. Description of the structures

ORTEP diagrams of complexes **10**, **16** and **22** are given in Figs. 2–4, respectively. Selected bond distances and angles for complexes **10** and **22** are given in Table 2. Selected bond distances and angles for complexes **16**, **18** and **21** are given in Table 3. The structure of **10**, as

shown in Fig. 2, is prototypical of '3 + 1' complexes with the $[MO]^{3+}$ core. The rhenium site exhibits distorted square pyramidal geometry with the basal plane defined by the two sulfur donors and the pyridine nitrogen donor of the NS_2 tridentate ligand and thiolate donor of the monodentate moiety and the apical position occupied by the oxygen group. The distorted five-coordinate geometry may be quantitatively evaluated by using the trigonality index, τ, described by Addison et al. [24]. The measurement uses the two largest angles contained in the mean basal plane, which expressed in the form $(\beta - \alpha)/60$ to give a unitless value ranging from 0 to 1 with $\tau = 0$ for perfect square pyramid, and $\tau = 1$ for ideal trigonal bipyramid. The τ indices for the rhenium mixed thiolate compounds of this study are listed in Table 4. The τ value for **10** is 0.147, which is much lower than common [SSS]/[S] and [SOS]/[S] complexes [25], but similar to those reported previously in this laboratory in the investigation of [ONS] Schiff base tridentate/monothiolate '3 + 1' complexes [7]. The rhenium atom is situated 0.742 Å above the basal plane defined by the four coordinated atoms.

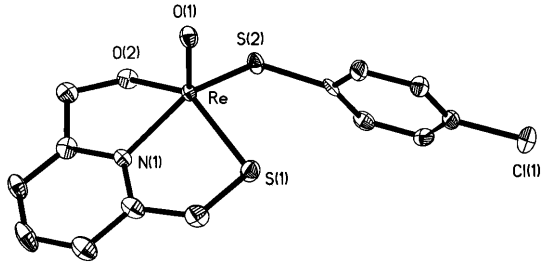

Fig. 3. ORTEP drawing of [ReO(η^3-$OCH_2C_5H_3NCH_2S$)(η^1-C_6H_4Cl-4-S)] (**16**). Ellipsoids corresponds to 50% probability.

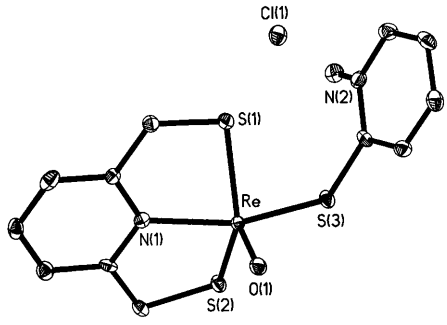

Fig. 4. ORTEP drawing of [ReO(η^3-$OCH_2C_5H_3NCH_2S$)(η^1-C_5H_4NH-2-S)][Cl] (**22**). Ellipsoids corresponds to 50% probability.

Table 4
The τ index for the five-coordinated rhenium complexes of this study, as a measurement of geometric distortion from idealized geometries

Complex	α [a]	β [b]	τ [c]
[ReO(S–N–S)(C_6H_4Br–4–S)] (**10**)	136.79	145.63	0.147
[ReO(O–N–S)(C_6H_4Cl-4-S)] (**16**)	136.49	141.10	0.077
[ReO(O–N–S)($C_6H_4OCH_3$-4-S)] (**18**)	138.10	141.00	0.048
[ReO(O–N–S)($C_6H_4OCH_3$-4-CH_2S)] (**21**)	136.16	142.88	0.112
[ReO(S–N–S)(C_5H_4NH-2-S)][Cl] (**22**)	136.38	147.81	0.191

[a] $\alpha \equiv$ the second largest basal plane, S1–Re–S2 for **10** and **22**, S1–Re–O2 for **16**, **18** and **21**.

[b] $\beta \equiv$ the largest basal plane, S3–Re–N1 for **10** and **22**, S2–Re–N1 for **16**, **18** and **21**.

[c] $\tau \equiv (\beta - \alpha)/60$. S–N–S = η^3-$SCH_2C_5H_3NCH_2S$ and O–N–S = η^3-$OCH_2C_5H_3NCH_2S$.

As shown in Fig. 4, the structure of [ReO(η^3-$SCH_2C_5H_3NCH_2S$)(η^1-C_5H_4NH-2-S)][Cl] (**22**) consists of discrete complex cations and charge balancing Cl^- anions. The nature of the ligand, specifically the steric requirement of the [SNS] tridentate ligand (**4**), the inability of the tridentate ligand to occupy the idealized equatorial positions while sterically blocking the sixth potential coordination position, possibly from the pyridyl nitrogen of potentially bidentate ligand, 2-mercaptopyridine, as well as the *trans* influence of the axial oxo-group, prohibits the formation of '3 + 2' complexation geometry [26]. In common with **10**, this cationic complex also has a slightly distorted square pyramidal coordination sphere for rhenium with a τ value close to 0.2 and out-of-plane distance of 0.726 Å defined by the mean plane of four [SNS]/[S] coordination atoms.

Complexes **16**, **18** and **21** are structurally identical except for the difference of monothiolate ligand. They all possess square pyramidal geometry with less distortion ($\tau < 0.12$) compared to those of [SNS]/[S] analogs mentioned above. The out-of-plane distances for rhenium from the basal plane of oxygen, nitrogen and two sulfur atoms are 0.742, 0.737, and 0.740 Å for **16**, **18** and **21**, respectively. The average bond lengths of Re=O, Re–O, Re–N and Re–S are 1.682, 2.015, 2.078 and 2.285 Å, respectively. All the Re–S bonds are identical within statistical limits. These values are agreement with those of analogous oxorhenium complexes observed [7].

4. Conclusions

We have described the synthesis of a number of novel '3 + 1' oxorhenium(V) complexes (**8**–**22**) using designed tridentate ligands [SNS] 2,6–dithiomethylpyridine (**4**) or [ONS] 6-thiomethyl-2-pyridinemethanol (**5**) in combination with *para*-substituted benzenethiol or *para*-substituted benzyl mercaptans. The 5-coordinated 16-electron complexes possess nearly ideal square pyramidal geometry. The series of complexes described here may be considered as mimics for tetrahydrochrysene (THC) and estradiol [27].

5. Supplementary material

All atomic and thermal parameters and all interatomic angles are available from the author upon request. Crystallographic data (excluding structure factor) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 139786 to 139790. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit @ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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