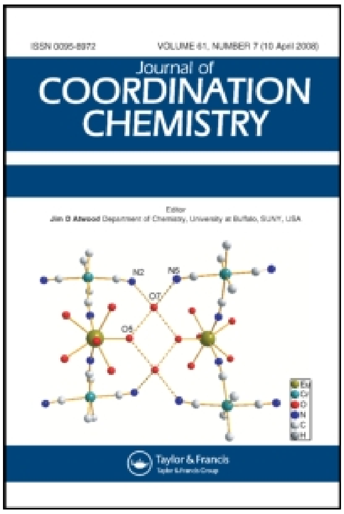

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Binary and ternary oxorhenium(V) complexes: synthesis, characterization, and crystal structure

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A series of anionic five-coordinate binary oxorhenium(V) complexes with dithiolato ligands, $Bu_4N[ReO(L^1)_2]$ (**1a**), $Bu_4N[ReO(L^2)_2]$ (**1b**), and $Bu_4N[ReO(L^3)_2]$ (**1c**), and a series of neutral octahedral ternary oxorhenium(V) complexes of mixed dithiolato and bipyridine ligands, $[ReO(L^1)(bpy)Cl]$ (**2a**), $[ReO(L^2)(bpy)Cl]$ (**2b**), and $[ReO(L^3)(bpy)Cl]$ (**2c**) (where L^1H_2 = ethane-1,2-dithiol, L^2H_2 = propane-1,3-dithiol, L^3H_2 = toluene-3,4-dithiol, and bpy = 2,2′-bipyridine), were isolated and characterized by physicochemical and spectroscopic methods. The solid state structure of **1c** was established by X-ray crystallography. All the mononuclear oxorhenium(V) complexes are diamagnetic. The redox behavior of all the complexes has been studied voltammetrically.

Keywords: Oxorhenium(V) complex; Dithiol ligand; Crystal structure

1. Introduction

Interest in coordination chemistry of rhenium and technetium complexes arises from the use of these compounds in diagnostic nuclear medicine and the need for new compounds with improved chemical and pharmaceutical properties [1–9]. Oxorhenium(V) complexes having a nitrogen–sulfur donor set play a role as potential candidates in nuclear medicine and the β-emitting isotopes ^{186}Re and ^{188}Re constitute the basis for radiopharmaceuticals [10–15]. Thus, neutral oxotechnetium(V) and oxorhenium(V) mixed ligand complexes are important due to their *in vitro* and *in vivo* stability in terms of oxidation state of the metal and ligand exchange [16–18].

Herein we report a series of binary oxorhenium(V) complexes with dithiols of type $Bu_4N[ReO(L)_2]$ (**1**), and new neutral ternary oxorhenium(V) complexes containing dithiols and bipyridine, $[ReO(L)(bpy)Cl]$ (**2**), as shown in scheme 1. All the complexes were isolated and characterized by physicochemical and spectroscopic tools, and finally the detailed structure of **1c** has been confirmed by single crystal X-ray crystallography.

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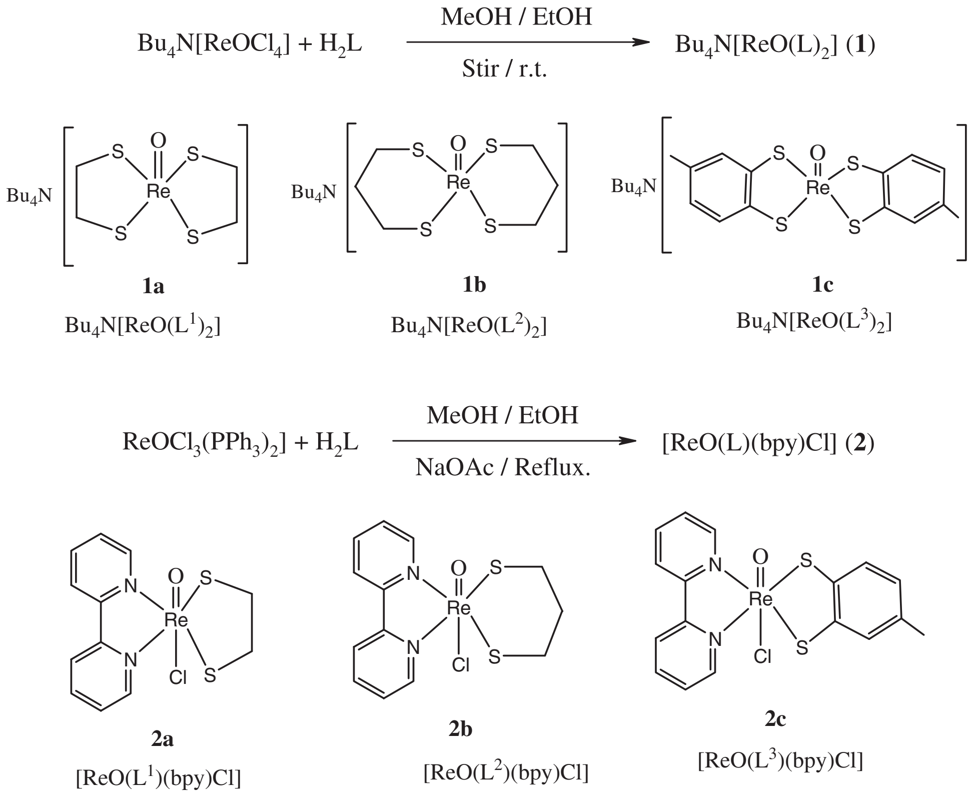

$$Bu_4N[ReOCl_4] + H_2L \xrightarrow[\text{Stir / r.t.}]{\text{MeOH / EtOH}} Bu_4N[ReO(L)_2]\ (\mathbf{1})$$

1a $Bu_4N[ReO(L^1)_2]$

1b $Bu_4N[ReO(L^2)_2]$

1c $Bu_4N[ReO(L^3)_2]$

$$ReOCl_3(PPh_3)_2] + H_2L \xrightarrow[\text{NaOAc / Reflux.}]{\text{MeOH / EtOH}} [ReO(L)(bpy)Cl]\ (\mathbf{2})$$

2a $[ReO(L^1)(bpy)Cl]$

2b $[ReO(L^2)(bpy)Cl]$

2c $[ReO(L^3)(bpy)Cl]$

Scheme 1. Synthetic routes and structural formulas of **1** and **2**.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals and reagents were obtained from commercial sources and used as received, unless otherwise stated. Solvents were distilled from an appropriate drying agent [19]. The precursors $Bu_4N[ReOCl_4]$ and $ReOCl_3(PPh_3)_2$ were prepared according to literature procedures [20, 21].

Elemental analyses (carbon, hydrogen, nitrogen, and sulfur) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. The electronic absorption spectra were recorded on a JASCO UV-Vis/NIR spectrophotometer model V-570 from 1100 to 200 nm. The IR spectra were obtained using a Perkin-Elmer FTIR model RX1 spectrometer in compressed KBr pellets. The ^{1}H-NMR spectra were recorded on a Bruker AC300 spectrometer using TMS as internal standard. Molar conductance (Λ_M) was measured in a Systronics 304 conductivity meter using $\sim 10^{-3}$ M solutions in acetonitrile. The electrochemical measurements were recorded on a computer controlled EG&G PAR model 270 VERSTAT electrochemical instrument using Ag/AgCl electrodes with TBAP as supporting electrolyte at 298 K in acetonitrile solution purged with dry dinitrogen and complex concentration of 10^{-3}–10^{-4} M.

2.2. *Preparation of the oxorhenium(V) complexes 1*

Oxorhenium(V) complexes **1** were synthesized following a common procedure, as described below, using $Bu_4N[ReOCl_4]$ and the respective dithiol compounds in 1 : 2 mole ratio. Ethane-1,2-dithiol (188 mg, 2.0 mM) (for complex **1a**), propane-1,3-dithiol (216 mg, 2.0 mM) (**1b**), and toluene-3,4-dithiol (312 mg, 2.0 mM) (**1c**) were mixed with 1.0 mM of $Bu_4N[ReOCl_4]$ and the mixture was stirred for half an hour in dry methanol/ethanol. The reaction mixture was then refluxed for 2 h. In each synthesis, the red complex precipitated and the solid was filtered after reduction of the solvent volume.

The pure crystallized product was obtained from dichloromethane solution of the products. Red single crystals of **1c** were obtained from dichloromethane–hexane (1 : 1).

$Bu_4N[ReO(C_2H_4S_2)_2]$ (1a): $C_{20}H_{44}NOReS_4$: Anal. Found: C, 38.31; H, 7.15; N, 2.15; S, 20.06; Calcd: C, 38.15; H, 7.05; N, 2.22; S, 20.36. IR (cm^{-1}): $\nu_{C\text{–}S}$, 745; $\nu_{Re=O}$, 954; $\nu_{Re\text{–}S}$, 450. ^1H-NMR (δ, ppm): 2.75 (s, 8H), 2.91 (br, m, 8H), 1.41 (m, 16H), 0.89 (t, 12H). Conductivity (Λ_o, $ohm^{-1}\,cm^2\,M^{-1}$) in acetonitrile: 139. Yield: 70–75%.

$Bu_4N[ReO(C_3H_6S_2)_2]$ (1b): $C_{22}H_{48}NOReS_4$: Anal. Found: C, 40.29; H, 7.39; N, 2.05; S, 19.67; Calcd: C, 40.20; H, 7.36; N, 2.13; S, 19.49. IR (cm^{-1}): $\nu_{C\text{–}S}$, 745; $\nu_{Re=O}$, 953; $\nu_{Re\text{–}S}$, 452. ^1H-NMR (δ, ppm): 2.46 (t, 8H), 2.82 (br, m, 8H), 1.75 (m, 4H), 1.32 (m, 16H), 0.80 (t, 12H). Conductivity (Λ_o, $ohm^{-1}\,cm^2\,M^{-1}$) in acetonitrile: 145. Yield: 55–60%.

$Bu_4N[ReO(C_7H_6S_2)_2]$ (1c): $C_{30}H_{48}NOReS_4$: Anal. Found: C, 47.62; H, 6.49; N, 1.80; S, 17.09; Calcd: C, 47.83; H, 6.43; N, 1.86; S, 17.01. IR (cm^{-1}): $\nu_{C\text{–}S}$, 746; $\nu_{Re=O}$, 957; $\nu_{Re\text{–}S}$, 453. ^1H-NMR (δ, ppm): 7.64 (d, 2H), 7.55 (s, 2H), 6.75 (d, 2H), 2.56 (t, 8H), 2.31 (s, 6H), 1.12 (m, 16H), 0.82 (t, 12H). Conductivity (Λ_o, $ohm^{-1}\,cm^2\,M^{-1}$) in acetonitrile: 135. Yield: 87–93%.

2.3. *Preparation of the oxorhenium(V) complexes 2*

$ReOCl_3(PPh_3)_2$ (830 mg, 1.0 mM) was added to a solution of sodium acetate (1.5 mM) in methanol/ethanol (15–20 mL). To this suspension, the respective dithiol compounds (1.0 mM) and bipyridine (156 mg, 1.0 mM) were added with stirring. The mixture was refluxed for 3 h. After cooling to room temperature, the volume of the reaction mixture was reduced and then diluted with dichloromethane and water. The organic layer was separated from the mixture and the volume of the solution was reduced to 10–12 mL. The slow evaporation of the solvents at room temperature afforded crystalline brown product.

$[ReO(C_2H_4S_2)(bpy)Cl]$ (2a): $C_{12}H_{12}ClN_2OReS_2$: Anal. Found: C, 29.34; H, 2.57; N, 5.62; S, 13.01; Calcd: C, 29.64; H, 2.49; N, 5.76; S, 13.17. IR (cm^{-1}): $\nu_{C=N}$, 1457; $\nu_{C\text{–}S}$, 749, $\nu_{Re=O}$, 961; $\nu_{Re\text{–}N}$, 532; $\nu_{Re\text{–}S}$, 453; $\nu_{Re\text{–}Cl}$ 326. ^1H NMR (δ, ppm): 8.69 (d, 2H), 8.41 (d, 2H), 7.72 (m, 2H), 6.99 (m, 2H), 2.87 (s, 4H). Conductivity (Λ_o, $ohm^{-1}\,cm^2\,M^{-1}$) in acetonitrile: 90. Yield: 55–60%.

$[ReO(C_3H_6S_2)(bpy)Cl]$ (2b): $C_{13}H_{14}ClN_2OReS_2$: Anal. Found: C, 31.69; H, 2.93; N, 5.54; S, 12.61; Calcd: C, 31.21; H, 2.82; N, 5.60; S, 12.80. IR (cm^{-1}): $\nu_{C=N}$, 1467; $\nu_{C\text{–}S}$, 746, $\nu_{Re=O}$, 956; $\nu_{Re\text{–}N}$, 528; $\nu_{Re\text{–}S}$, 450; $\nu_{Re\text{–}Cl}$ 324. ^1H-NMR (δ, ppm): 8.61 (d, 2H), 8.44 (d, 2H), 7.65 (m, 2H), 7.04 (m, 2H), 2.61 (t, 4H), 1.93 (m, 2H). Conductivity (Λ_o, $ohm^{-1}\,cm^2\,M^{-1}$) in acetonitrile: 86. Yield: 52–55%.

[ReO($C_7H_6S_2$)(bpy)Cl] (2c): $C_{17}H_{14}ClN_2OReS_2$: Anal. Found: C, 37.49; H, 2.51; N, 4.99; S, 11.42; Calcd: C, 37.24; H, 2.57; N, 5.11; S, 11.68. IR (cm^{-1}): $\nu_{C=N}$, 1462; $\nu_{C–S}$, 752, $\nu_{Re=O}$, 960; $\nu_{Re–N}$, 531; $\nu_{Re–S}$, 455; $\nu_{Re–Cl}$ 327. ^{1}H-NMR (δ, ppm): 8.81 (d, 2H), 8.64 (d, 2H), 7.75 (m, 2H), 7.68 (d, 1H), 7.59 (s, 1H), 7.21 (m, 2H), 6.68 (d, 1H), 2.31 (s, 3H). Conductivity (Λ_o, $ohm^{-1}\,cm^2\,M^{-1}$) in acetonitrile: 87. Yield: 60–62%.

2.4. *X-ray crystal structure analysis*

The crystal data and details of data collection and refinement for **1c** are summarized in table 1. The diffraction data were collected at room temperature on a Nonius DIP-1030H system using Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell refinement, indexing, and scaling of all the data sets were performed using Denzo and Scalepack programs [22]. The structure was solved by direct methods and subsequent Fourier analyses [23], and refined by full-matrix least squares based on F^2 with all observed reflections. The contribution of H atoms at calculated position was included in the final cycles of refinement. In one dithiol ligand the methyl group was found disordered over two positions; both methyl carbons, C14 and C14b, were refined anisotropically with occupancies of 0.56(1) and 0.44(1), respectively. Calculations were performed using the WinGX System, version 1.70.01 [24].

3. Results and discussion

3.1. *Synthesis and characterization*

Complexes **1a** and **1c** have already been reported [25], but the procedure followed for their synthesis is different from that reported here and the synthetic procedure was

Table 1. Crystallographic data and processing parameters for **1c**.

Empirical formula	$C_{30}H_{48}NOReS_4$
Formula weight	753.13
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions (Å, °)	
a	9.390(2)
b	17.648(3)
c	20.378(4)
α	90.0
β	98.63(3)
γ	90.0
Volume (Å^3), Z	3338.7(11), 4
Calculated density ($g\,cm^{-3}$)	1.498
$F(000)$	1528
θ range for data collection (°)	1.53–26.37
μ (Mo-Kα) (mm^{-1})	3.912
Total reflections	6792
Observed reflections	4341
Goodness-of-fit on F^2	0.896
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0373$, $wR_2 = 0.0887$
R indices (all data)	$R_1 = 0.0624$, $wR_2 = 0.0960$
Largest difference peak and hole (e Å^{-3})	0.737 and –0.775

not common for these two complexes (scheme 1). The synthesis of **1a** was carried out in inert atmosphere and that of **1c** was performed with several steps. If the synthetic procedure differs from that described [25], another six-coordinate oxorhenium(V) complex of L^3, $[ReO(L^3)_2(H_2O)]$, is obtained [26].

Here, we have a common procedure for synthesis of the five-coordinate oxorhenium(V) complexes of general formula $Bu_4N[ReO(L)_2]$ (**1**) by allowing the dithiol (LH_2) to react with the oxorhenium(V) precursor, $Bu_4N[ReOCl_4]$, in methanolic/ethanolic medium without inert atmosphere. As a result, we obtained a new complex, $Bu_4N[ReO(L^2)_2]$ (**1b**), belonging to this series. The crystal structure of **1c** has never been reported. The preparation of new mixed ligand complexes **2** was carried out by refluxing $[ReOCl_3(PPh_3)_2]$, bipyridine, and respective dithiol compounds (1 : 1 : 1 mole ratio) in methanol/ethanol containing sodium acetate.

The oxorhenium(V) complexes (**1** and **2**) are stable and soluble in common organic solvents except ether and hexane. The microanalytical data and spectroscopic data of **1** along with the X-ray crystallographic results of **1c** indicate that these complexes are five-coordinate anionic oxorhenium(V) species with dithiolato ligands. Complexes **2** are mixed ligand octahedral oxorhenium(V) complexes of *S,S′*-dithiolato, *N,N′*-bipyridine, and chloride. Complexes **1** are 1 : 1 electrolytes as the observed conductivity (Λ_o) for these complexes are in the range of 135–145 $\mathrm{ohm^{-1}\,cm^2\,M^{-1}}$ in acetonitrile, whereas conductivities (Λ_o) of *ca* 86 $\mathrm{ohm^{-1}\,cm^2\,M^{-1}}$ in acetonitrile for **2** indicate non-electrolytes. All the complexes are diamagnetic.

3.2. *Structure of 1c*

The crystal of **1c** comprises Bu_4N^+ cations and $[ReO(L^3)_2]^-$. The atom-numbering scheme is depicted in figure 1, while a selection of bond lengths and angles are tabulated in table 2. The complex has a distorted square pyramidal geometry with the oxo-ligand apical and two 3,4-dimercapto toluene anions in the basal plane.

Here, three Re–S bond distances are comparable within their ESDs (mean 2.317(1) Å) while Re–S(4) is slightly shorter (2.3079(14) Å). Distortion from ideal is indicated by the displacement of the metal (0.73 Å) from the S4 mean basal plane toward the oxo ligand. But more remarkable is the dihedral angle calculated through the Re/S1/S2 and Re/S3/S4 planes, of 50.81(5)°. The angle formed by the toluene rings is 22.9(2)°. The Re=O distance, 1.670(3) Å, agrees with values found in other oxorhenium compounds. The RX structural analysis indicates disorder of the methyl group in one of the ligands leading to a *cis* and *trans* geometrical configuration of the complex of *ca* same percentage. The refined occupation is 0.56(1)/0.44(1) for C14 and C14b, respectively. The present metal geometry as well as the coordination distances are similar to those found in [bis(benzene-1,2-dithiolato)-oxorhenium(V)] complexes structurally characterized asPPh_4^+, NEt_4^+, and NBu_4^+ salts [27–29].

3.3. *Spectroscopic properties*

The IR spectra of all the complexes clearly differentiate between **1** and **2**. Peaks around 953(s), 745(s) and 450(w) $\mathrm{cm^{-1}}$, attributable to the stretching frequency of $\nu_{Re=0}$, $\nu_{C–S}$, and $\nu_{Re–S}$, respectively, are present in all complexes. On the other hand, peaks at *ca* 1465 (m), *ca* 530 (w), and *ca* 323 (w) $\mathrm{cm^{-1}}$, corresponding to $\nu_{C=N}$, $\nu_{Re–N}$ and $\nu_{Re–Cl}$, respectively [15], are present in **2** only, indicating the presence of bpy and chloride in the coordination sphere.

The electronic spectra of all complexes (**1** and **2**) in acetonitrile were recorded at room temperature. The UV–Vis spectral data of **1** are in accord with previously reported data [25]. The characteristic broad weak absorption for all the ReO(V) complexes was observed around 490 nm along with the strong absorption bands below 400 nm.

^{1}H-NMR spectra of **1** clearly indicate the presence of the n-Bu_4N^+ group and the integration ratio between the n-Bu_4N^+ and dithiolato ligand signals shows a molar ratio of 1 : 2, as supported by conductivity. In the ^{1}H-NMR spectra of **2**, no signal for n-Bu_4N^+ is present, as expected; new signals in the aromatic region corresponding to bipyridine were observed in addition to signals of thiolate. This observation and the other physicochemical and spectral data indicate the presence of bipyridine and thiolate in the coordination sphere of ReO(V). The ratio of the integrated signals for bipyridine and thiolate is 1 : 1.

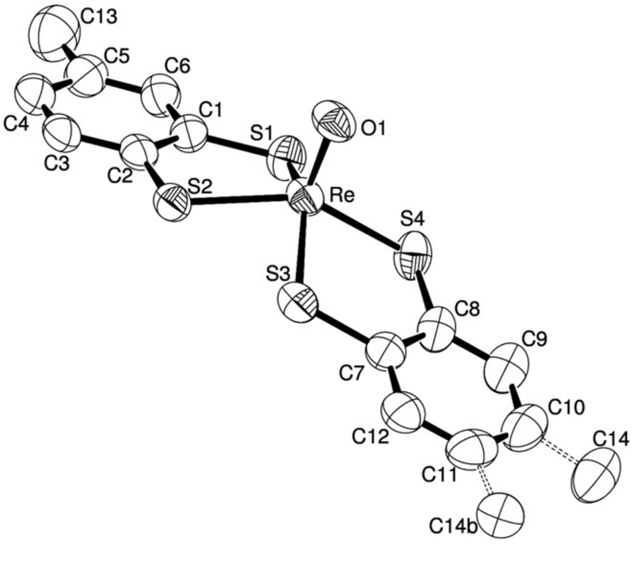

Figure 1. ORTEP of $Bu_4N[ReO(L^3)_2]$ (**1c**) (H-atoms are not shown for clarity). One methyl is disordered over two positions (C14/C14b of 0.56/0.44 occupancy) corresponding to a *cis* and *trans* configuration of the complex.

Table 2. Selected bond lengths (Å) and angles (°) for **1c**.

Bond lengths (Å)		Bond angles (°)			
Re–O1	1.670(3)	O1–Re–S1	108.57(13)	S1–Re–S3	142.33(5)
Re–S1	2.3166(14)	O1–Re–S2	108.25(12)	S1–Re–S4	83.83(6)
Re–S2	2.3186(14)	O1–Re–S3	109.10(13)	S2–Re–S3	83.55(6)
Re–S3	2.3175(16)	O1–Re–S4	107.95(13)	S2–Re–S4	143.80(5)
Re–S4	2.3079(14)	S1–Re–S2	84.75(6)	S3–Re–S4	84.84(6)

3.4. *Electrochemistry*

The electrochemical properties of all complexes have been studied by cyclic voltammetry in acetonitrile (0.1 M TBAP). The voltammetric data are given in table 3. The voltammograms showed a Re^{IV}/Re^{V} redox couple in **1**, whereas a Re^{V}/Re^{VI} couple was observed in the mixed ligand oxorhenium complexes **2**. One-electron, quasi-reversible reduction behavior occurring at E1/2 of *ca* −0.70 V *versus* SCE attributable to Re(V)/Re(IV) reduction in **1** along with no oxidative response has been obtained. Complexes **2** show an oxidative response on the positive side of SCE assignable to Re(V)–Re(VI) oxidation [30] along with no reduction for rhenium(V) to rhenium(IV). One-electron stoichiometry of these responses has been established by comparing their current heights with those of standard ferrocene/ferrocenium couple under identical experimental conditions.

Voltammetric parameters are studied by varying the scan rate (ν) from 50 to 400 mVs^{-1}. The ratio between the cathodic peak current (I_{pc}) and the square root of the scan rate ($I_{pc}/\nu^{1/2}$) is almost constant. The peak potential shows a slight dependence with the scan rate (ν). It can be concluded that the redox couple is related to a quasi-reversible, one-electron transfer controlled by diffusion.

4. Conclusion

A facile procedure not requiring inert atmosphere has been used to prepare binary oxorhenium(V) complexes of dithiolato ligands (L) in high yield (**1**) and a new oxorhenium(V) complex (**1b**) has been obtained. The reaction of 2,2′-bipyridine with the $[Re^{V}O]^{3+}$ core of $ReOCl_3(PPh_3)_2$ in the presence of dithiolates and sodium acetate led to the isolation of neutral six-coordinate complexes ReO(bpy)(L) (**2**). In the two instances, different oxorhenium precursors and syntheses have been used to obtain the desired complexes. The geometry of the five-coordinate complexes **1** is different from that of recently published five-coordinate binary oxorhenium(V) complex of N,N donor sets [31], as here the structures of **1** show a distorted square-pyramidal geometry with the oxo-ligand at apical position, but in the reported oxorhenium(V) complex [31] rhenium lies in a distorted trigonal-bipyramidal environment. New mixed ligand octahedral complexes **2** are different from the recently reported octahedral

Table 3. UV-Vis spectral and electrochemical data.

		Electrochemical data[a] $E^{\circ\prime}, V$ (ΔE_p, mV)	
Compound	λ nm (ε)[a] (ε, $dm^3 M^{-1} cm^{-1}$)	Re(V)/Re(IV)	Re(V)/Re(VI)
1a	–	−0.65 (220)	–
1b	–	−0.73 (240)	–
1c	–	−0.55 (180)	–
2a	230(11,756), 256(10,592), 332(5,204), 492 (42)	–	+0.71 (220)
2b	232(11,313), 283(10,638), 322(3,259), 489(33)	–	+0.73 (240)
2c	238(13,096), 306(7,142), 360(5,612), 500(65)	–	+1.35 (100)

[a] In acetonitrile.

oxorhenium(V) complexes of pentadentate N_3O_2 donor ligands [32] and β-diketonate systems [33] in terms of the donor sets, though in all complexes the pharmaceutically important ReO^{3+} moiety is present. The tendency for rhenium(V) in **1** to reduce to Re(IV) and to oxidize to Re(VI) in **2** has been observed voltammetrically, and the redox behavior is in accordance with the electronic nature of the ligands present in coordination sphere.

Supplementary material

Crystallographic data for **1c** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 714739. The copies of this information are available on request and free of charge from CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax +44-122-3336033; Email: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).

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