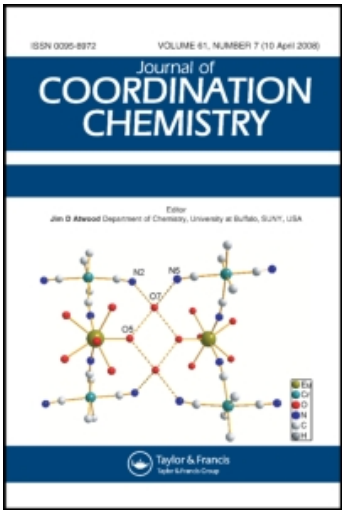

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A synthetic route to cationic '3 + 2' oxorhenium(V) complexes containing imidazole derivatives

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The neutral complex $[ReOBr_2(tmi)]$ [Htmi = 2-(1-ethanolthiomethyl)-1-methylimidazole] was synthesized by reaction of $(n\text{-}Bu_4N)[ReOBr_4(OPPh_3)]$ with an equimolar amount of Htmi in acetonitrile. The '3 + 2' complex [ReO(tmi)(mi)]Cl [Hmi = 2-(hydroxymethyl)-1-methylimidazole] was isolated from a one-pot reaction of $(n\text{-}Bu_4N)[ReOCl_4]$ with Htmi and Hmi in equimolar quantities in acetonitrile. The compounds were characterized by spectroscopic methods and X-ray crystallography. Both complexes have distorted octahedral geometries with the alcoholate oxygen of tmi coordinated *trans* to the oxo group.

Keywords: Oxorhenium(V); Crystal structure; Didentate; Terdentate

1. Introduction

One of the approaches to synthesize stable monooxorhenium(V) complexes for possible application as therapeutic radiopharmaceuticals has been the '3 + 2' concept of ligand permutation [1]. This is based on the ligation of a dinegative tridentate chelate in combination with a bidentate monoanionic ligand to produce neutral octahedral monooxorhenium(V) complexes. We have recently become involved in the synthesis of rhenium complexes with multidentate ligands containing the imidazole group. It has been shown that the reaction of the *N*,*S*-donor bidentate 2-(1-ethylthiomethyl)-1-methylimidazole (etmi) with *trans*-$[ReOCl_3(PPh_3)_2]$ under argon leads to the formation of $[ReOCl(OEt)(etmi)(PPh_3)]Cl$ [2]. However, in air the binuclear species $[(\mu\text{-}O)\{ReOCl_2(etmi)\}_2]$ is formed [3]. With the *N*,*O*-donor bidentate ligand 2-(hydroxymethyl)-1-methylimidazole (Hmi), reaction led to $[ReOCl_2(mi)(PPh_3)]$ [4]. We have now "combined" the etmi and Hmi ligands in the *N*,*S*,*O*-donor tridentate 2-(1-ethanolthiomethyl)-1-methylimidazole (Htmi), the

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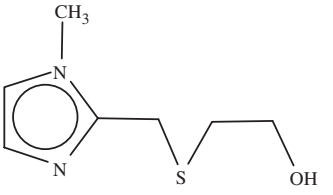
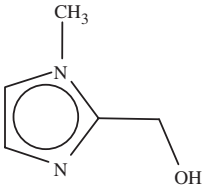
reaction of which with (n-Bu_4N)[$ReOCl_4$] or (n-Bu_4N)[$ReOBr_4(OPPh_3)$] leads to the neutral monomers [$ReOX_2$(tmi)] (X = Cl, Br) (**1**). It was found that reaction of complexes **1** with the potentially monoanionic bidentate ligand Hmi does not lead to the monocationic '3 + 2' complex [ReO(tmi)(mi)]X (**2**), which could only be prepared in pure form by a one-pot procedure involving **1** and the ligands.



Htmi



Hmi

2. Experimental

(n-Bu_4N)[$ReOCl_4$] and (n-Bu_4N)[$ReOBr_4(OPPh_3)$] were prepared by literature procedures [5, 6]. Hmi was prepared by a literature method [7]. Scientific instrumentation used is the same as reported elsewhere [2]. Solvents were purified and dried before use. Laboratory chemicals were of reagent grade and used without further purification. Infrared spectra were obtained using KBr disks and ^{1}H NMR spectra were run in d_6-DMSO.

2.1. Syntheses

2.1.1. Htmi. A mass of 5 g (30 mmol) of 2-chloromethyl-1-methylimidazole [6] was dissolved in 20 cm^3 of ethanol and K_2CO_3 (6.2 g, 45 mmol) added. To this mixture was added a solution of 2.34 g of 2-mercaptoethanol (30 mmol) dissolved in 20 cm^3 of ethanol, and the mixture was heated at reflux was continued for an hour. After cooling to room temperature, the solution was stirred overnight, after which a white precipitate (KCl) was filtered off. Ethanol was then removed under reduced pressure, leaving a brown oil. The oil was taken up in 50 cm^3 of chloroform, more KCl filtered off, and the solution was dried with anhydrous sodium sulfate. On removal of the chloroform by rotary evaporation, a yellow oil was obtained and which was distilled under vacuum. Its boiling point was 167°C at 5 mTorr. Yield: 78%. ^{1}H NMR: 6.90 (d, 1H, H(1)); 6.84 (d, 1H, H(2)); 3.88 (s, 2H, C(4)H_2); 3.80 (t, 2H, C(6)H_2); 3.65 (s, 3H, C(7)H_3); 2.68 (t, 2H, C(5)H_2).

2.1.2. [$ReOBr_2$(tmi)] (1b). (n-Bu_4N)[$ReOBr_4(OPPh_3)$] (100 mg, 96 μmol) was dissolved in 10 cm^3 of acetonitrile and an equimolar amount of Htmi (17 mg), dissolved in 5 cm^3 of acetonitrile was added dropwise with stirring at room temperature. The solution was then heated to reflux for 30 min, and after cooling to room temperature it was filtered. The solution was then left to evaporate slowly at room temperature, continuously depositing violet crystals, which were suitable for X-ray analysis. Yield: 69%; m.p. 279°C. Anal. Calcd for $C_7H_{11}N_2O_2SBr_2Re$ (%): C, 15.77; H, 2.08; N, 5.25. Found: C, 16.11; H, 2.22; N, 4.98. IR: ν(Re=O) 949(vs);

ν(Re–N) 513(m); ν(Re–O) 470(m); ν(Re–S) 266. ^{1}H NMR: 7.66 (s, 1H, *H*(1)); 7.60 (s, 1H, *H*(2)); 4.17 (s, 2H, C(4)H_2); 3.82 (s, 3H, C(7)H_3); 3.32 (t, 2H, C(6)H_2); 2.63 (t, 2H, C(5)H_2). [$ReOCl_2$(tmi)] (**1a**) was prepared in the same manner by using (n-Bu_4N)[$ReOCl_4$] as starting material.

2.1.3. [ReO(tmi)(mi)]Cl (2a). Equimolar amounts of Hmi (19 mg, 174 μmol) and Htmi (29 mg) dissolved in 8 cm^3 of acetonitrile were added slowly to an acetonitrile solution of (n-Bu_4N)[$ReOCl_4$] (100 mg, 170 μmol). The mixture was heated at reflux for 1 h, after which the violet solution was cooled to room temperature. It was filtered, and 2 cm^3 of DMF added. Slow evaporation at room temperature led to the formation of violet crystals, which were suitable for X-ray diffraction studies. Yield: 78%; m.p. 298°C. Anal. Calcd for $C_{12}H_{18}N_4O_3SClRe \cdot 2H_2O$ (%): C, 25.92; H, 3.99; N, 10.08. Found: C, 25.82; H, 4.01; N, 10.12. IR: ν(Re=O) 946(vs); ν(Re–N) 521(m), 571(m); ν(Re–O) 471(m); ν(Re–S) 270. ^{1}H NMR: 7.75 (d, 1H, *H*(8)); 7.70 (s, 2H, *H*(1)*H*(9)); 7.47 (d, 1H, *H*(2)); 4.52 (s, 2H, C(4)H_2); 4.78 (s, 2H, C(11)H_2); 3.94 (s, 3H, C(14)H_3); 3.88 (s, 3H, C(7)H_3); 3.33 (t, 2H, C(6)H_2); 2.92 (t, 2H, C(5)H_2).

2.2. X-ray *crystallography*

X-ray diffraction studies of crystals of **1b** and **2a** were performed using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation

Table 1. Crystal data and structure refinement details for **1b** and **2a**.

	1b	**2a**
Chemical formula	$C_7H_{11}N_2O_2SBr_2Re$	$C_{12}H_{18}N_4O_3SClRe \cdot 2H_2O$
Formula weight	533.26	556.05
Temperature (K)	200(2)	200(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimension (Å, °)	$a = 8.3073(7)$	6.7442(1)
	$b = 11.612(1)$	26.5871(4)
	$c = 13.086(1)$	10.1320(2)
	$\beta = 94.08(1)$	91.3670(5)
Volume (Å^3)	1259.1(2)	1816.24(5)
Z	4	4
Density (calc.) (mg m^{-3})	2.813	2.034
Absorption coefficient (mm^{-1})	16.146	6.982
F(000)	976	1080
Crystal size (mm)	0.23 × 0.35 × 0.50	0.02 × 0.15 × 0.20
θ range (°)	2.3–28.0	3.4–25.1
Index ranges	$-10 \le h \le 10$; $-15 \le k \le 15$; $-17 \le \ell \le 17$	$-7 \le h \le 8$; $-31 \le k \le 31$; $-12 \le \ell \le 12$
Reflections measured	10 651	18 386
Independent reflections	2838	3197
Observed data [$I > 2\sigma(I)$]	2398	2767
Data/parameters	2838/137	3197/229
Goodness-of-fit on F^2	0.96	1.04
Final R indices	0.0254, $wR2 = 0.0592$	0.0255, $wR2 = 0.0558$
Largest diff. peak/hole (e Å^{-3})	1.76/−1.15	0.89/−1.08

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

1b		**2a**	
Re–O(2)	1.699(4)	Re–O(3)	1.698(3)
Re–O(1)	1.935(4)	Re–O(1)	1.946(3)
Re–Br(1)	2.5140(6)	Re–O(2)	1.960(3)
Re–Br(2)	2.5324(6)	Re–N(3)	2.087(3)
Re–S	2.456(1)	Re–S	2.475(1)
Re–N(1)	2.095(4)	Re–N(1)	2.106(3)
S–C(5)	1.800(6)	S–C(5)	1.804(5)
O(1)–C(6)	1.415(7)	O(1)–C(6)	1.404(5)
C(1)–N(1)	1.382(7)	C(1)–N(1)	1.373(5)
S–C(4)	1.823(5)	S–C(4)	1.831(5)
C(3)–N(1)	1.341(7)	C(3)–N(1)	1.339(6)
C(3)–N(2)	1.334(7)	C(3)–N(2)	1.335(6)
O(2)–Re–O(1)	163.8(2)	O(3)–Re–O(1)	164.7(1)
O(2)–Re–Br(1)	102.2(1)	O(3)–Re–O(2)	104.7(1)
O(2)–Re–Br(2)	97.3(1)	O(3)–Re–N(3)	94.8(1)
O(2)–Re–S	85.3(1)	O(3)–Re–S	86.7(1)
O(2)–Re–N(1)	92.2(2)	O(3)–Re–N(1)	92.9(1)
Br(1)–Re–Br(2)	89.41(2)	O(2)–Re–N(3)	79.9(1)
O(1)–Re–S	79.1(1)	O(1)–Re–S	78.1(1)
S–Re–N(1)	81.7(1)	S–Re–N(1)	80.8(1)
Re–O(1)–C(6)	127.6(3)	Re–O(1)–C(6)	130.1(2)
Re–N(1)–C(3)	119.9(3)	Re–N(1)–C(3)	121.4(3)

($\lambda = 0.71073$ Å). Further details are given in table 1, with selected bond lengths and angles in table 2. The structures were solved by direct methods. Non-hydrogen atoms were refined with anisotropic displacement parameters. Structural refinements were made by the full-matrix least-squares method on F^2 using the program SHELXL-97 [8].

3. Results and discussion

3.1. Synthesis

In addition to using (n-Bu_4N)[$ReOCl_4$], which complicates synthetic procedures due to its moisture sensitivity, we have used (n-Bu_4N)[$ReOBr_4(OPPh_3)$] as starting complex because of its stability and the ease of substitution of its bromide and $OPPh_3$ ligands. They both react with equimolar quantities of Htmi in acetonitrile to give [$ReOX_2$(tmi)] (X = Cl (**1a**), Br(**1b**)) as products. Due to the viscosity of the oily Htmi ligand, acetonitrile was found to be the only common solvent to be used as a reaction medium. Due to the propensity of rhenium(V) to form neutral complexes, the potentially bidentate monoanionic ligand Hmi was used in efforts to synthesize '3 + 2' cationic oxorhenium(V) complexes. However, difficulties were experienced in the reactions of [$ReOX_2$(tmi)] with Hmi, which either led to the recovery of the starting materials or to impure decomposition products. Therefore, a simple one-pot procedure involving either $[ReOCl_4]^-$ or $[ReOBr_4(OPPh_3)]^-$ with equimolar quantities of Htmi and Hmi led to the isolation of [ReO(tmi)(mi)]X (**2**). Complexes **2** are diamagnetic and are 1 : 1 electrolytes in DMF. They are soluble in most polar solvents.

3.2. Spectroscopy

In IR spectra, the Re=O stretches of **1** and **2** appear as sharp strong bands in the narrow range 945–950 cm^{-1}, which fall in the region normally observed for six-coordinate rhenium(V) complexes containing N-, S- and O-donor ligands [3, 4, 9]. Spectra of **1b** and **2a** show that coordination of tmi takes place through the unsaturated nitrogen atom of the imidazole ring, the sulfur atom and the deprotonated alcoholate oxygen. This is indicated by the change in frequency of the C=N stretching band upon formation of the complex. In ring systems, ν(C=N) is usually observed at about 1650 cm^{-1} [10]. Chelation of Htmi to Re(V) results in a lowering of the frequency of the band from 1647 cm^{-1} in the free ligand to 1616 cm^{-1} in **1b** (1619 and 1629 cm^{-1} in **2a**). The ν(Re–N) mode is evidenced by a medium absorption at 513 cm^{-1} (521 and 571 cm^{-1} in **2a**). Coordination of the alcoholate oxygen atom is indicated by the lowering of $\nu(CH_2–O)$ from 1248 cm^{-1} in the free ligand to 1207 cm^{-1} in **1b** (1198 and 1211 cm^{-1} in **2a**). A band of medium intensity at 266 and 270 cm^{-1} in the spectra of **1b** and **2a**, respectively, is assigned to ν(Re–S).

The complexes show sharp, well-resolved peaks in their ^{1}H NMR spectra, which unambiguously establish the presence of the chelates. There are no detectable paramagnetic shifts or line broadening of the signals. Proton signals of the imidazole ring in **1b** are practically identical with the two rings in **2a**, while signals of the methylene protons in **2a** show a small downfield shift relative to those in **1b**.

3.3. Crystal *structures*

The structure of **1b** is illustrated in figure 1. It consists of a discrete, monomeric and neutral oxorhenium(V) [$ReOBr_2$(tmi)] molecules packed with no intermolecular contacts shorter than the sum of van der Waals radii. The coordination geometry around rhenium is highly distorted octahedral; the nitrogen and sulfur atoms of the tridentate uninegative N(1)SO(1)-donor ligand lie on the equatorial

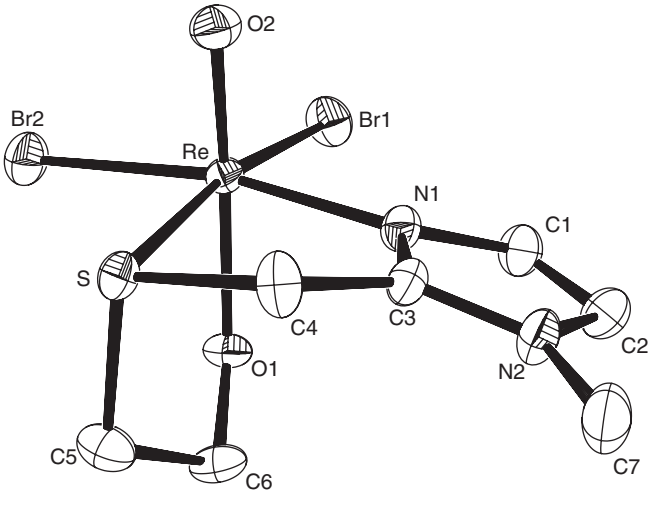


Figure 1. An ORTEP view of [$ReOBr_2$(tmi)] (**1b**) showing the atom labelling scheme and 40% probability ellipsoids.

plane, along with the two *cis*-bromides, while the alcoholate O(1) atom is *trans* to the O(2) oxo atom. The equatorial plane is strictly planar, with the rhenium atom displaced by 0.185 Å towards O(2). This displacement leads to the angles O(2)–Re–Br(1) = 102.2(1), O(2)–Re–Br(2) = 97.3(1), O(2)–Re–N(1) = 92.2(2) and O(2)–Re–S = 85.3(1)°. The distortion results in a nonlinear O(1)–Re–O(2) axis of 163.8(2)°, accomplished by Br(1)–Re–S and Br(2)–Re–N(1) angles of 171.02(4) and 169.4(1)°, respectively. The two 'bite' angles of tmi, N(1)–Re–S = 81.7(1) and S–Re–O(1) = 79.(1)°, contribute considerably to this distortion. Re lies 1.075 Å from the Br(1)Br(2)O(2) plane and 1.412 Å from the N(1)SO(1) plane, the angle between the two triangular faces being 7.83°. Interligand angles in the equatorial plane depart markedly from the ideal value of 90° (81.7 to 94.5°). The imidazole ring is planar, as expected for an aromatic system, with torsion angles C(3)N(2)C(2)C(1) = 0.5(6) and N(1)C(1)C(2)N(2) = 0.4(7)°. The bond angle around C(4) is 110.5(4)°, and the N(1)C(3)C(4)S torsion angle is 25.1(7)°. The axial Re–O(1) bond (1.935(4) Å) is longer than those found for Re–O(ethoxide) bonds, and indicates significant double bond character [2]. Another indication of its double bond character is that the Re–O(1)–C(6) angle is splayed to 127.6(3)° when no apparent intramolecular non-bonding contacts exist. Bond lengths in the inner core show no unusual features, being within the range expected by comparison to other similar monooxorhenium(V) complexes [2–4].

In the mononuclear complex **2a** (figure 2) the coordination geometry around the rhenium(V) is also distorted octahedral; the two imidazole nitrogens, the sulfur and O(2) atoms lie on the equatorial plane, with the alcoholate O(1) atom of the tridentate tmi ligand *trans* to the O(3) oxo atom. The O(1)–Re–O(3) axis is nonlinear (164.7(1)°), and the rhenium atom is displaced from the mean equatorial plane by 0.170 Å towards O(3), resulting in the angles O(3)–Re–O(2) = 104.7(1), O(3)–Re–N(3) = 94.8(1), O(3)–Re–S = 86.7(1) and O(3)–Re–N(1) = 92.9(1)°. Both 'bite' angles N(1)–Re-S (80.8(1)°) and O(1)–Re–S (78.2(1)°) are smaller than in **1b**. The bite angle of the mi ligand is 79.9(1)°, considerably less than the Br(1)-Re-Br(2) angle of 89.41(2)° in **1b**. In the O_3N_2S polyhedron the Re atom lies 1.003 Å from the N(3)O(2)O(3) plane and 1.387 Å from the N(1)SO(1) plane, the dihedral angle being 12.5°. There is little deviation from planarity of the tmi imidazole ring, with C(3)N(2)C(2)C(1) and N(1)C(1)C(2)N(2) torsion angles being 0.1(5) and −0.6(5)°, respectively. There is a delocalised double

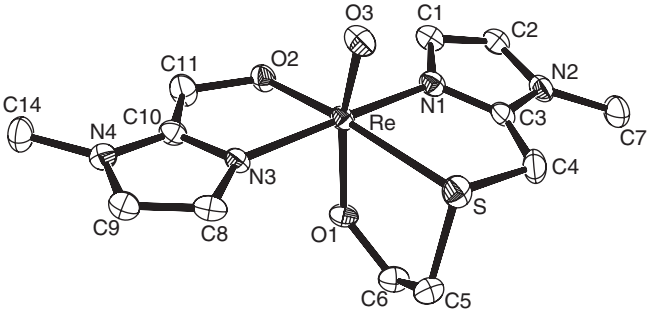


Figure 2. Molecular structure and atom numbering scheme for [ReO(tmi)(mi)]Cl (**2a**). Hydrogen atoms have been omitted for clarity.

bond over the N(1)C(3)N(2) part of the ring, with bonds N(1)–C(3) = 1.339(6) and N(2)–C(3) = 1.335(6) Å. The bond angle C(3)C(4)S = 111.4(3)° and the N(1)C(3)C(4)S torsion angle equals 4.4(6)°. Axial Re–O(3) (1.698(3) Å) and Re–O(1) (1.946(3) Å) bond lengths are nearly identical to those in **1b**. The difference between the Re–N(1) (2.106(3) Å) and Re–N(3) (2.087(3) Å) bond lengths is not significant, and is similar to this kind of bond in **1b**. Surprisingly, the Re–O(1) bond (*trans* to the oxo group) is shorter than Re–O(2) (1.960(3) Å). The Re–O(1)–C(6) bond angle (130.1(2)°) is markedly bigger than in **1b**.

We have previously [11] prepared the complex $[ReOCl_2(L)]$, where L^- is an ONN-donor ligand containing a phenolate oxygen, a secondary amino nitrogen and a pyridyl nitrogen as donor atoms [HL = 2-[[{2-(2-pyridinyl)ethyl}amino]methyl]-phenol]. The phenolate oxygen occupies the site *trans* to the oxo group, with the two chlorides in *cis* positions. Efforts to prepare '3 + 2' complexes by reaction of $[ReOCl_2(L)]$ with the O,O-donors 1,2-dihydroxybenzene (H_2cat) and oxalic acid (H_2ox) were unsuccessful. However, the complexes [ReO(L)(cat)] and [ReO(L)(ox)] could easily be prepared by one-pot reactions of $[ReOCl_4]^-$ with HL and H_2cat/H_2ox.

Supplementary data

Files CCDC 270179 (for **1b**) and CCDC 270180 (for **2a**) contain the crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving/html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223-336033; email: deposit@ccdc.cam.ac.uk.

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