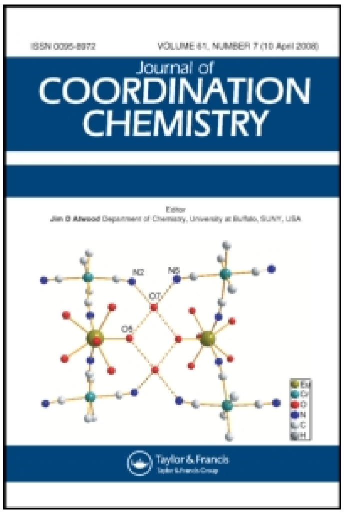

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Synthesis and characterization of a cationic oxorhenium(V) complex containing the pentadentate N_3O_2-donor ligand <i>bis</i>(<i>N</i>-methylsalicylideneiminopropyl)amine

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Synthesis and characterization of a cationic oxorhenium(V) complex containing the pentadentate N_3O_2-donor ligand *bis*(*N*-methylsalicylideneiminopropyl)amine

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The complex salt $[ReO(bsa)]PF_6$ ($H_2bsa = $ *bis*(*N*-methylsalicylideneiminopropyl)amine) was prepared from the reaction of *cis*-$[ReO_2I(PPh_3)_2]$ with H_2bsa in toluene. The dianionic pentadentate ligand bsa is coordinated to the ReO^{3+} moiety via one secondary amino and two imino nitrogens, and two anionic phenolate oxygens. The complex was characterized by spectroscopy and analytical data, and the structure has been determined by single-crystal X-ray diffraction analysis.

Keywords: Oxorhenium(V); Pentadentate N_3O_2-donor; Crystal structure

1. Introduction

Interest in coordination chemistry of rhenium originates from potential application of complexes of ^{186}Re and ^{188}Re as therapeutic agents in nuclear medicine, and in catalysis [1]. One approach to synthesize stable oxorhenium(V) complexes is the employment of a mixed-ligand set of a dinegative tridentate chelate in combination with an uninegative monodentate or bidentate ligand to produce neutral "3 + 1" and "3 + 2" mixed ligand complexes containing the robust ReO^{3+} core [2–4]. We recently used the "4 + 1" approach to prepare complexes containing multidentate imidazole derivatives [5].

We are interested in preparing mononuclear cationic oxorhenium(V) complexes for radiopharmaceutical applications [5–9]. In this study, we decided to use the pentadentate Schiff base ligand H_2bsa (*bis*(*N*-methylsalicylideneiminopropyl)amine), which can act as a potential dianionic N_3O_2 chelate, to yield a cationic "5 + 0"

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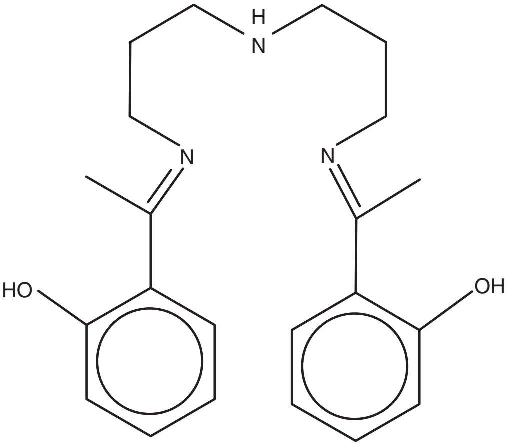
oxorhenium(V) complex of the formula [ReO(bsa)]PF_6 (**1**). Although neutral complexes of oxorhenium(V)



H_2bsa

with penta- and tetradentate Schiff bases are common, cationic species are rare in the literature. The neutral rhenium(V) and technetium(V) complexes [ReO(apa)] and [TcOCl(epa)] were prepared from the potentially pentadentate N_3O_2-donor ligand *N*,*N*′-3-azapentane-1,5-diyl-*bis*{3-(1-iminoethyl)-6-methyl-2*H*-pyran-2,4-(3*H*)-dione} (H_3apa) and the potentially tetradentate N_2O_2-donor ligand *N*,*N*′-ethylenediyl-*bis*-{3-(1-iminoethyl)-6-methyl-2*H*-pyran-2,4-(3*H*)-dione} (H_2epa) [10].

2. Experimental

2.1. *Reactants and methods*

Reagent-grade NH_4ReO_4 and deuterated solvents were purchased from Aldrich. Solvents and other chemicals (Aldrich) were used as received. *cis*-[$ReO_2I(PPh_3)_2$] was prepared according to a literature procedure [11]. The ligand *bis*(*N*-methylsalicylideneiminopropyl)amine was prepared by a literature procedure [12]. The scientific instrumentation used is the same as reported elsewhere [13]. The infrared spectrum was obtained in a KBr disc and the ^{1}H NMR spectrum was run in d_6-DMSO.

2.2. *Synthesis*

2.2.1. [ReO(basa)]PF_6 (1). [$ReO_2I(PPh_3)_2$] (0.103 g, 0.118 mmol) and 0.044 g of H_2bsa (0.120 mmol) were added to toluene (15 cm^3), and the mixture was heated under reflux to give a green solution. After 1 h NH_4PF_6 (0.020 g, 0.122 mmol) was added, and heating was continued for another 2 h. After cooling to room temperature, the solution was filtered, and left to evaporate slowly at room temperature for 3 days to yield green crystals, which were removed by filtration, washed with ethanol and acetone, and dried under vacuum. Yield = 0.054 g (64% based on Re), m.p. =201°C. Anal. Calcd for $ReC_{22}H_{27}N_3O_3PF_6$ (%): C, 37.08; H, 3.82; N, 5.90. Found: C, 37.21; H, 4.02; N, 5.98. IR (ν_{max}/cm^{-1}): 3185 (N–H), 1614 (C=N), 940 (Re=O), 849 (P–F), 555, 544 (Re–N),

Table 1. Crystal data and structure refinement data for **1**.

Chemical formula	$C_{22}H_{27}N_3O_3RePF_6$
Formula weight	712.64
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	7.0468(1)
b	22.5825(5)
c	15.9979(4)
β	102.324(1)
Volume (Å^3)	2487.15(9)
Z	4
Density (Calcd) (mg m^{-3})	1.903
Absorption coefficient (mm^{-1})	5.025
$F(000)$	1392
Crystal size (mm)	0.01 × 0.05
θ range for data collection (°)	3.2–27.1
Index ranges	$-8 \le h \le 9$, $-28 \le k \le 28$, $-20 \le l \le 18$
Reflections measured	45384
Independent/observed reflections	5484/4026
Data/parameters	5484/325
Goodness of fit on F^2	1.05
Final R indices [$I > 2\sigma(I)$]	0.0329 ($wR_2 = 0.0693$)
Largest diff. peak and hole (e Å^3)	1.54, −0.73

419, 398 (Re–O). ^{1}H NMR (δ ppm): 7.66 (d, 2H, $J = 8$ Hz, $H2$, $H21$), 7.28 (t, 2H, $J = 8$ Hz, $H4$, $H19$), 7.15 (t, 1H, $J = 8$ Hz, $H3$), 6.79 (d, 2H, $J = 8$ Hz, $H5$, $H18$), 6.72 (t, 1H, $J = 8$ Hz, $H20$), 3.63 (t, 4H, $J = 6.7$ Hz, 2x $H9$, 2x $H14$), 2.97 (t, 4H, $J = 6.7$ Hz, 2x $H11$, 2x $H12$), 1.94 (quintet, 4H, $J = 6.7$ Hz, $H10$, $H13$), 2.29 (s, 3H, C(8)H_3), 1.89 (s, 3H, C(16)H_3). UV-vis (λ_{max}, nm/ε, M^{-1} cm^{-1}): 388 (9900), 313 (42000). Conductivity (10^{-3} M, DMF): 91 ohm^{-1} cm^2 mol^{-1}.

2.3. *Crystallography*

Diffraction data were measured with a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation and the ω-scan technique. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 software [14]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in calculated positions. A summary of crystal data and structure refinement is given in table 1. Some selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis and spectral characterization*

The complex [ReO(bsa)]PF_6 (**1**) was obtained from reaction of *cis*-[$ReO_2I(PPh_3)_2$] with an equimolar quantity of H_2bsa in toluene, with addition of NH_4PF_6 to isolate the cationic complex:

$$ReO_2I(PPh_3)_2 + H_2bsa + NH_4PF_6 \rightarrow \mathbf{1} + 2PPh_3 + H_2O + NH_4I$$

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

Re–O(3)	1.678(4)	Re–O(2)	1.999(3)
Re–O(1)	1.952(3)	Re–N(3)	2.173(4)
Re–N(1)	2.124(4)	Re–N(2)	2.089(4)
N(1)–C(7)	1.307(6)	N(2)–C(15)	1.300(6)
N(3)–C(11)	1.491(6)	N(3)–C(12)	1.505(7)
O(2)–C(22)	1.343(6)	O(1)–C(1)	1.334(6)
N(1)–C(9)	1.484(6)	N(2)–C(14)	1.482(6)
O(3)–Re–O(2)	169.1(2)	O(1)–Re–N(3)	166.5(2)
N(1)–Re–N(2)	167.4(2)	O(1)–Re–N(1)	90.3(1)
N(1)–Re–N(3)	97.6(2)	N(2)–Re–N(3)	87.2(2)
N(2)–Re–O(2)	82.3(1)	O(3)–Re–O(1)	103.0(1)
O(3)–Re–N(1)	93.9(2)	O(3)–Re–N(2)	98.0(2)
O(3)–Re–N(3)	87.4(2)	O(1)–Re–O(2)	87.9(1)
Re–O(2)–C(22)	122.7(3)	C(11)–N(3)–C(12)	108.7(4)
C(7)–N(1)–C(9)	117.5(4)	C(14)–N(2)–C(15)	121.0(4)
C(6)–C(7)–C(8)	117.5(4)	N(2)–C(15)–C(17)	121.4(4)

The conductivity of **1** in DMF ($\Lambda_M = 91\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$) confirms that it is a 1 : 1 electrolyte. Conductivity readings between 65 and 90 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ are consistent with 1 : 1 electrolytes in DMF [15]. The complex is soluble in the most polar solvents such as DMSO, DMF and acetonitrile, and is stable for months in the solid state, and for days in solution.

The infrared spectrum of **1** displays the Re=O stretching frequency as a medium intensity peak at 940 cm^{-1}. The C=N stretches, which appear at 1613 cm^{-1} in the free ligand, are shifted to 1597 cm^{-1} in **1**. Two weak absorptions at 419 and 398 cm^{-1} are assigned to the Re–O stretching vibrations. The peak due to the N–H stretch shifted from 3295 cm^{-1} in the free ligand to 3185 cm^{-1} in the complex. The presence of the PF_6^- counterion is established unequivocally by a very strong absorption at 849 cm^{-1} which dominates the spectrum. The absorption at 555 cm^{-1}, and the shoulder at 544 cm^{-1}, are assigned to ν(Re–N(1)/N(3)) and ν(Re–N(3)), respectively. In the ^{1}H NMR spectrum the two-proton signal that appears the furthest downfield at 7.66 ppm is ascribed to *H*2/*H*21. Although the two phenyl rings are magnetically inequivalent, a two-proton triplet (at 7.28 ppm) for H4/H19 and a two-proton doublet for *H*5/*H*18 at 6.79 ppm are observed. However, two separate triplets are observed for *H*3 (at 7.15 ppm) and *H*20 (at 6.72 ppm). The protons on C(10) and C(13) are magnetically equivalent and give rise to a four-proton quintet at 1.94 ppm, as are the protons on C(9)/C(14) (triplet at 3.63 ppm) and on C(11)/C(12) (triplet at 2.97 ppm). The two methyl groups C(8)H_3 and C(16)H_3 give rise to two singlets at 2.29 and 1.89 ppm. The electronic spectrum of **1** reveals an intra-ligand (bsa) transition at 313 nm, while a ligand-to-metal charge transfer band is observed at 388 nm.

3.2. *Crystal structure*

A perspective view of the asymmetric unit of $[ReO(bsa)]^+$ is shown in figure 1. The complex exhibits a distorted octahedral geometry around the central rhenium(V), with the basal plane being defined by the phenolate oxygen O(1), the two imino

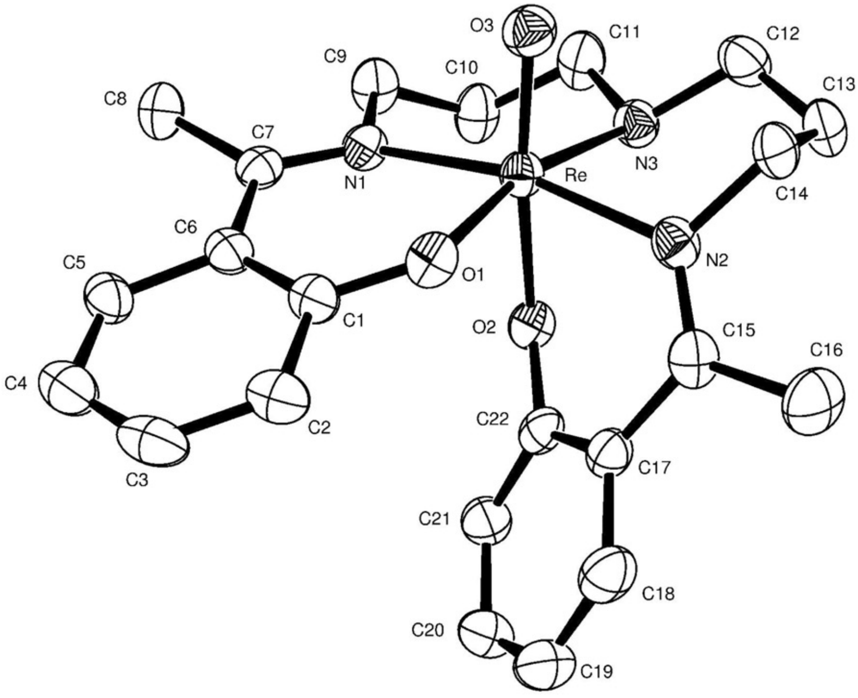


Figure 1. Structure of $[ReO(bsa)]^+$ with the atom numbering scheme and thermal ellipsoids drawn at 40% probability. The hydrogen atoms are omitted for clarity.

nitrogens N(1) and N(2), and the secondary amino N(3). The oxo group O(3) and phenolate O(2) lie in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(2)–Re–O(3) axis of 169.1(2)°, accomplished by O(1)–Re–N(3) and N(1)–Re–N(2) angles of 166.5(2) and 167.4(2)°, respectively. The metal is shifted out of the mean equatorial plane by 0.103 Å towards O(3), the result of the non-orthogonal angles O(3)–Re–N(1) = 93.9(2)°, O(3)–Re–N(2) = 98.0(2)°, O(3)–Re–N(3) = 87.44(2)° and O(3)–Re–O(1) = 103.0(2)°. Surprisingly, the bite angles N(1)–Re–N(3) [97.6(2)°] and N(3)–Re–N(2) [87.2(2)°] differ significantly. The other two bite angles of the pentadentate bsa ligand are O(1)–Re–N(1) = 90.3(1)° and N(2)–Re–O(2) = 82.3(1)°.

The Re–O(3) distance of 1.678(4) Å implies some triple bond character and is typical of cationic complexes of this kind [5–9]. The Re–O(2) bond [1.999(3) Å] is, as expected, longer than Re–O(1) [1.952(3) Å], due to the large *trans* effect of the oxo O(3). Both these distances fall within the observed range of 1.92(2)–2.09(2) Å for Re–O (phenolate) bonds [2, 7, 9]. The significant difference in the Re–N (imine) bond lengths [Re–N(1) = 2.124(4) Å, Re–N(2) = 2.089(4) Å] may be due to the steric and angular strain in the ligand backbone. The Re–N(3) distance of 2.173(4) Å is typical of Re(V)–N (amine) bonds [9, 16].

Both the N(1)–C(7) [1.307(6) Å] and N(2)–C(15) [1.300(6) Å] bonds are double, and the C(7)–N(1)–C(9) [117.5(4)°] and C(14)–N(2)–C(15) [121.0(4)°] bond angles are close to the ideal of 120° for a sp^2-hybridized nitrogen. The C(11)–N(3)–C(12) angle of 108.7(4)° illustrates the sp^3 hybridization of the secondary amino N(3).

Table 3. Hydrogen-bonding geometry (Å, °).

D	H	A	D–H	H···A	D···A	∠D–H···A
N3	H3	F3	0.93	2.26	3.14(1)	156.0
C3	H3A	F1	0.95	2.51	3.39(1)	154.2
C10	H10B	F2	0.99	2.55	3.34(1)	137.4
C11	H11A	F1	0.99	2.45	3.29(1)	142.0
C13	H13A	F4	0.99	2.46	3.44(1)	168.2
C14	H14B	O3	0.99	2.52	3.04(1)	112.0
C18	H18	F2	0.95	2.38	3.26(1)	154.3

The packing of the complex in the unit cell is complemented by several hydrogen-bonds involving the PF_6^- counterion (see table 3), in addition to the intramolecular hydrogen bond C(14)–H(14B)···O(3).

In earlier work, we prepared the cationic '3 + 2' rhenium(V) complex [ReO(tmi)(mi)]Cl [Htmi = 2-(1-ethanolthiomethyl)-1-methylimidazole; Hmi = 2-(hydroxymethyl)-1-methylimidazole] from the reaction of $[ReOCl_4]^-$ with equimolar quantities of Htmi and Hmi [6]. However, the reaction of $[ReOCl_4]^-$ with the tetradentate Schiff base ligand 1,2-benzylene-*bis*(salicylideneimine) [H_2sal_2mp] gave the neutral distorted octahedral complex [$ReOCl(sal_2mp)$] [17].

Supplementary data

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC) with a deposition number of CCDC-625522. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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