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Schiff base chemistry of the $\{\text{ReO}\}^{3+}$ core: structural characterization of the unusual '3 + 2' complex $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{-CH=NC}_6\text{H}_4\text{-2-S})(\eta^2\text{-OC}_6\text{H}_4\text{-NC}_6\text{H}_4\text{-2-S})]$

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Abstract

The reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with salicylaldehyde-2-mercaptoanil (**1**) in methanol yields $[\text{ReO}(\text{OCH}_3)(\text{PPh}_3)(\eta^3\text{-OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{S})]$ (**3**). Reaction of **3** with 2-(2-hydroxyphenyl)benzothiazole (**2**) produces $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{S})(\eta^2\text{-OC}_6\text{H}_4\text{-NC}_6\text{H}_4\text{S})]$ (**4**) in good yield. Compound **4** may also be prepared directly from the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with excess **1**, after prolonged reaction times in the presence of atmospheric oxygen. The structure of **3** exhibits a distorted octahedral Re(V) center coordinated to a terminal oxo-group, a methoxy ligand, a triphenylphosphine ligand, and the N, O and S donors of the tridentate Schiff base ligand. The octahedral geometry of **4** is defined by the terminal oxo-group, the N, O and S donors of the tridentate Schiff base ligand, and the N and O donors of the bidentate 2-(2-hydroxyphenyl)benzothiazole ligand. Oxidation and cyclization of the Schiff base salicylaldehyde-2-mercaptoanil to produce 2-(2-hydroxyphenyl)benzothiazole is precedented and in this instance may be driven by the formation of the robust '3+2' complex **4**.

Keywords

Crystal structures; Oxorhenium complexes; Schiff base complexes

1. Introduction

The development of rhenium coordination chemistry has gained significant impetus from the potential applications of the radioisotopes ^{186}Re and ^{188}Re to radiotherapy [1–5]. One approach to the design of novel reagents has focused on polydentate ligands with thiolate and nitrogen donors with the robust $\{\text{ReO}\}^{3+}$ core [6]. The '3+1' concept of ligand addition provides a strategy for the consistent synthesis of $\{\text{ReO}\}^{3+}$ core complexes, allowing a systematic investigation of the size, shape, molecular weight, and charge of the rhenium-thiolate complexes [7–10]. The concept is based on ligation of a dinegative tridentate unit with the (S-X-Y^-) donor set ($\text{X} = \text{O}, \text{S}, \text{NR}$; $\text{Y} = \text{S}, \text{O}$) in combination with a mononegative thiol, so as to preserve the oxometal core and the formal +5 oxidation state of the metal. More recently, the '3+1' concept has been extended to Schiff base ligands with (O–N–S) donor groups, a strategy which provides a general and facile method for high yield synthesis of robust complexes with the $\{\text{ReO}\}^{3+}$ core [11].

As part of these investigations on Schiff base materials of the $\{\text{ReO}\}^{3+}$ unit, we have studied the stepwise addition of salicylaldehyde-2-mercaptoanil, $\text{HOC}_6\text{H}_4\text{-CH=NC}_6\text{H}_4\text{SH}$ (**1**), to $[\text{ReOCl}_3(\text{PPh}_3)_2]$ to yield $[\text{ReO}(\text{OCH}_3)(\text{PPh}_3)(\eta^3\text{-OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{S})]$ (**3**) and $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{S})(\eta^2\text{-OC}_6\text{H}_4\text{C(=NC}_6\text{H}_4\text{S)})]$ (**4**). Compound **4** is an example of a '3+2' complex of the $\{\text{ReO}\}^{2+}$ core [12,13] in which one ligand is present in the tridentate open chain imine form, while the second has been oxidized to the bidentate 2-(2-hydroxyphenyl) benzothiazole form.

2. Experimental

2.1. General considerations

NMR spectra were recorded on a Bruker DPX 300 (^1H 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. Ammonium perrhenate, salicylaldehyde and 2-aminobenzenethiol were purchased from Aldrich and used without further purification. Reagent grade solvents, distilled and dried by standard methods, were used in all cases. $[\text{ReOCl}_3(\text{PPh}_3)_2]$ was prepared according to the literature [14]. Schiff base salicylaldehyde-2-mercaptoanil (**1**) was prepared previously in this laboratory [13] and by Corbin and Work [15]. 2-(2-Hydroxyphenyl)benzothiazole (**2**) was synthesized according to a reported procedure [16].

2.2. Preparation of $\text{ReO}(\text{OCH}_3)(\text{PPh}_3)[\eta^3\text{-O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-2-S}]$ (**3**)

To a solution of Schiff base **1** (23 mg, 0.1 mmol) in CHCl_3 (20 cm^3) was added $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (83 mg, 1 mmol) and subsequently Et_3N (mg, mmol). The resulting solution was refluxed for 10 min and MeOH (10 cm^3) was then added, and the red solution was refluxed for further 10 min. The reaction mixture was evaporated to dryness under reduced pressure. The brick-red residue was washed with ice-cold MeOH ($2 \times 5 \text{ cm}^3$) (yield: 47 mg, 65%). IR (KBr, cm^{-1}): 968, $\nu(\text{Re=O})$. ^1H NMR (CDCl_3 , ppm): 3.49 (s, 3H, OCH_3), 7.3 (s, 15H, PPh_3), 7.4–7.9 (m, 8H, ArH). Anal. Calc. for $\text{C}_{32}\text{H}_{27}\text{NO}_3\text{PSRe}$: C, 53.19; H, 3.74; N, 1.94. Found: C, 53.36; H, 3.68; N, 2.01%. Red crystals suitable for X-ray crystallography were obtained by recrystallization from $\text{CHCl}_3\text{--MeOH}$.

2.3. Preparation of the '3+2' complex $[\text{ReO}(\eta^3\text{-O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-2-S})(\eta^2\text{-O-C}_6\text{H}_4\text{-C=N-C}_6\text{H}_4\text{-2-S})]$ (**4**)

2.3.1. Method A—From the intermediate $[\text{ReO}(\text{OCH}_3)(\text{PPh}_3)(\eta^3\text{-O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-2-S})]$ (**3**). To a solution of **3** (15 mg, 0.02 mmol) in CHCl_3 was added 2-(2-hydroxyphenyl)benzothiazole (5 mg, 0.022 mmol) and Et_3N (1 drop) was refluxed for 15 min, whereupon the color changed from red to dark brown. The solution was evaporated to dryness, rinsed with EtOH and Et_2O . This was dissolved in a small portion of CHCl_3 and purified over a silica gel column, using CHCl_3 and then 80/20 $\text{CHCl}_3/\text{acetone}$ as the eluent. X-ray quality crystals were obtained from recrystallization from CH_3CN (yield: 8 mg, 61%). IR (KBr, cm^{-1}): 963, $\nu(\text{Re=O})$. ^1H NMR (CDCl_3 , ppm): 7.45–7.55 (m, 4H, ArH), 7.65–7.75 (m, 4H, ArH). Anal. Calc. for $\text{C}_{26}\text{H}_{17}\text{N}_2\text{O}_3\text{S}_2\text{Re}\cdot\text{CH}_3\text{CN}$: C, 48.28; H, 2.87; N, 6.03. Found: C, 48.49; H, 2.78; N, 6.17%.

2.3.2. Method B—One-pot synthesis from $[\text{ReOCl}_3(\text{PPh}_3)_2]$. A mixture of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (83 mg, 0.1 mmol), Schiff base **1** (35 mg, 0.15 mmol), NaOAc (83 mg, 1 mmol) in MeOH (20 cm^3) and CHCl_3 (5 cm^3) was refluxed overnight. $\text{ReOCl}_3(\text{PPh}_3)_2$ dissolved slowly and the yellowish green solution turned to red and finally dark brown. The solvent was evaporated and the residue crystallized from CH_3CN (yield: 74%).

2.4. X-ray crystallography

Crystallographic data for **3** and **4** were collected with a Siemens P4 diffractometer equipped with the SMART CCD system [17] and using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) (Table 1). The data were collected at 89 K. The data were corrected for Lorentz and polarization effects, and absorption corrections were made using *SADABS* [18]. The structure solutions and refinements were carried out using the *SHELXL96* [19] software package. The structures were solved using direct methods and all of the non-hydrogen atoms were located from the initial solution. After locating all of the non-hydrogen 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 $\Delta/\sigma_{\text{max}}$ 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 $\Delta/\sigma_{\text{max}}$ was again less than 0.001.

3. Discussion

The ligand salicylaldehyde-2-mercaptoanil (**1**) is synthesized in the condensation reaction of 2-hydroxybenzaldehyde and 2-aminothiophenol (Scheme 1). Prolonged reaction times and exposure to oxygen results in the formation of 2-(2-hydroxyphenyl)benzothiazole (**2**) as a minor product. Compound **2** may be prepared directly as a monophasic material from the reaction of 2-cyanophenol and 2-aminophenylthiol (Scheme 2) [16].

The reaction of ligand **1** with $[\text{ReOCl}_3(\text{PPh}_3)_2]$ in methanol yields $[\text{ReO}(\text{OCH}_3)(\text{PPh}_3)(\eta^3\text{-OC}_6\text{H}_4\text{-CH=NC}_6\text{H}_4\text{S})]$ (**3**) in good yield. Subsequent reaction of **3** with 2-(2-hydroxyphenyl)benzothiazole **2** yields the '3+2' complex $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{-CH=NC}_6\text{H}_4\text{S})(\eta^2\text{-OC}_6\text{H}_4\text{-C=NC}_6\text{H}_4\text{S})]$ (**4**) (Scheme 3). Compound **4** could also be prepared directly from the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and **1** in the presence of sodium acetate and prolonged reaction times. This suggests that oxidation and ring closure of the open chain imine into the benzothiazole form is facilitated by introducing adventitious oxygen and extending the duration of the reaction.

The structure of **3**, shown in Fig. 1, consists of discrete distorted octahedral molecules. The coordination geometry at the rhenium(V) site is defined by the terminal oxo-group, the oxygen donor of a methoxo ligand, the phosphorus of the PPh_3 group, and the N, O and S donors of the tridentate Schiff base ligand. It is noteworthy that the oxo-group of **3** does not exert a significant *trans* influence, as indicated by the Re–O distance of 1.904 Å to the *trans* oxygen of the methoxy group (Table 2). The relatively long bond distances associated with the equatorial plane, defined by the N, O and S donors of the tridentate ligand and the P donor of the PPh_3 may reflect steric congestion along the molecular girdle.

As shown in Fig. 2, the structure of **4** consists of molecular oxorhenium(V) monomers. The distorted octahedral geometry of the Re(V) center is defined by the terminal oxo-group, the N, O and S donors of the tridentate Schiff base ligand, and the N and O donors of the bidentate 2-(2-hydroxyphenyl)benzothiazole ligand. Once again, it is noted that the Re–O3 distance along the axial vector O1–Re–O3 is significantly shorter than the Re–O2 distance in the equatorial plane, defined by O2, N1, S1 and N2 (1.989(3) and 2.076(3) Å, respectively). The N1–C7 distance of 1.330(6) Å and the valence angles at N1 of 118.6(4), 121.4(3) and 119.3(3)° confirm that the N1 site is sp^2 hybridized and the ligand in the Schiff base form. Similarly, the N2–C20 distance of 1.330(6) Å and the valence angles at N2 of 111.0(4), 124.1(3) and 124.7(3)° are consistent with an N2–C20 double bond and sp^2 hybridization at the N2 site, confirming that the bidentate ligand is in the oxidized 2-(2-hydroxy-phenyl)-benzothiazole form (Table 3).

4. Conclusions

Tridentate Schiff bases with mixed O, N, S donor groups provide effective chelates for the preparation of complexes with the $\{\text{ReO}\}^{3+}$ core. Most significantly, the oxorhenium-Schiff base structural unit may be exploited to prepare both '3+1' and '3+2' complexes depending on the identity of the coligand. Thus, $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{CH=N-C}_6\text{N}_4\text{S})(\eta^2\text{-OC}_6\text{H}_4\text{C}\equiv\text{NC}_6\text{H}_4\text{S})]$ (**4**) may be prepared from $[\text{ReO}(\text{OCH}_3)(\text{PPh}_3)(\eta^3\text{-OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{S})]$ (**3**) and 2-(2-hydroxyphenyl)-benzothiazole or directly from $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and the Schiff base salicylaldehyde-2-mercaptoanil. These results suggest that the Schiff base chemistry of the $\{\text{ReO}\}^{3+}$ core may be used to develop a diverse chemistry of materials whose size, shape, molecular weight, and charge may be systematically varied.

5. Supplementary material

All atomic and thermal parameters and all interatomic angles are available from the authors upon request. Crystallographic data (excluding structure factor) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as publication Nos. CCDC 140064 and 139496. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EQ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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References

1. Volkert W, Goeckeler WF, Ehrhardttrig GJ. Nucl. Med 1991;32:174.
2. DiZio JP, Fiaschi R, Davison A, Jones AG, Katzenellenbogen JA. Bioconj. Chem 1991;2:353.
3. Deutsch, EA.; Libson, K.; Vanderheyden, J-L. Technetium and Rhenium in Chemistry and Nuclear Medicine. Nicolini, M.; Bandoli, G.; Mazzi, U., editors. Vol. 3. New York: Raven Press; 1990. p. 13-22.
4. Volkert WA, Hoffman TJ. Chem. Rev 1999;99:2269. [PubMed: 11749482]
5. Schubiger PA, Alberto R, Smith A. Bioconj. Chem 1996;7:165.
6. Breitz H, Ratliff B, Schroff R, Vanderheyden J-L, Fritzberg AR, Appelbaum J, Fisher DR, Abrams P, Weiden P. J. Nucl. Med 1990;31:725.
7. Pietzsch HJ, Spies H, Hoffman S, Stach J. Inorg. Chim. Acta 1989;161:15.
8. Spies H, Fietz T, Pietzsch HJ, Johannsen B, Leibnitz P, Reck G, Scheller D, Klostermann K. J. Chem. Soc., Dalton Trans 1995:227. and references. therein.
9. Papadopoulos M, Pirmettis I, Tsoukalas C, Nock B, Maina T, Raptopoulou CP, Pietzsch H-J, Friebe M, Spies H, Johannsen B, Chiotellis E. Inorg. Chim. Acta 1999;295:1.
10. Maresca KP, Bonavia GH, Babich JW, Zubieta J. Inorg. Chim. Acta 1999;284:252. and references. therein.
11. Femia FJ, Chen X, Babich JW. J. Zubieta, Inorg. Chim. Acta 2000;300-302:517.
12. Nock B, Maina T, Tisato F, Papadopoulos M, Raptopoulou CP, Terzis A, Chiotellis E. Inorg. Chem 1999;38:4197.
13. Femia FJ, Babich JW, Zubieta J. Inorg. Chim. Acta 2000;300-302:462.
14. Chatt J, Rowe GA. J. Chem. Soc 1962:4019.
15. Corbin JL, Work DE. Can. J. Chem 1974;52:1054.
16. Shuter E, Hoveyda HR, Karunaratne V, Rettig SJ, Orwig C. Inorg. Chem 1996;35:368. [PubMed: 11666217]

17. Siemens, SMART Software Reference Manual. Madison, WI: Siemens Analytical X-ray Instruments; 1994.
18. Sheldrick, GM. SADABS: Program for Empirical Absorption Corrections. Germany: University of Göttingen; 1996.
19. Sheldrick, GM. SHELXL96, Program for the Refinement of Crystal Structures. Germany: University of Göttingen; 1996.

Fig. 1.
A view of the structure of **3**, showing the atom labeling scheme and 50% thermal ellipsoids.

Fig. 2.
A view of the structure of 4, showing the atom labeling scheme and 50% thermal ellipsoids.

Scheme 1.

Scheme 2.

Scheme 3.

Table 1

Summary of crystallographic data for [ReO(OCH₃)(PPh₃)(η³-OC₆H₄CH=NC₆H₄S)] (**3**) and [ReO(η³-OC₆H₄CH=NC₆H₄S)(η²-OC₆H₄C=NC₆H₄S)] (**4**)

	3	4
Empirical formula	C ₃₂ H ₂₇ NO ₃ PSRe	C ₂₈ H ₂₀ N ₃ O ₃ S ₂ Re
FW	722.78	696.79
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
Unit cell parameters		
<i>a</i> (Å)	19.454(7)	13.0575(6)
<i>b</i> (Å)	9.097(3)	16.5260(7)
<i>c</i> (Å)	31.37(1)	22.841(1)
β (°)	96.85(1)	90.00
<i>V</i> (Å ³)	5513(3)	4928.9(4)
<i>Z</i>	8	8
<i>D</i> _{calc} (g cm ⁻³)	1.742	1.878
μ (cm ⁻¹)	45.77	51.38
<i>R</i> ₁ ^a	0.0658	0.0338
<i>wR</i> ₂	0.1309	0.0618

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

Table 2Selected bond lengths (Å) and angles (°) for [ReO(OCH₃)(PPh₃)(η³-OC₆H₄CH=NC₆H₄S)] (**3**)

Re(1)–O(1)	1.707(8)	O(1)–Re(1)–O(3)	168.6(4)
Re(1)–O(3)	1.904(9)	O(1)–Re(1)–O(2)	87.8(4)
Re(1)–O(2)	2.114(9)	O(3)–Re(1)–O(2)	81.6(4)
Re(1)–N(1)	2.13(1)	O(1)–Re(1)–N(1)	95.9(4)
Re(1)–S(1)	2.306(4)	O(3)–Re(1)–N(1)	88.4(4)
Re(1)–P(1)	2.473(4)	O(2)–Re(1)–N(1)	89.8(4)
Re(2)–O(4)	1.711(8)	O(1)–Re(1)–S(1)	99.0(3)
Re(2)–O(6)	1.897(9)	O(3)–Re(1)–S(1)	91.9(3)
Re(2)–N(2)	2.15(1)	O(2)–Re(1)–S(1)	171.6(3)
Re(2)–O(5)	2.16(1)	N(1)–Re(1)–S(1)	84.8(3)
Re(2)–S(2)	2.311(4)	O(1)–Re(1)–P(1)	88.6(3)
Re(2)–P(2)	2.461(4)	O(3)–Re(1)–P(1)	87.5(3)
		O(2)–Re(1)–P(1)	91.9(3)
		N(1)–Re(1)–P(1)	175.3(3)
		S(1)–Re(1)–P(1)	93.1(1)
		O(4)–Re(2)–O(6)	166.7(4)
		O(4)–Re(2)–N(2)	94.8(4)
		O(6)–Re(2)–N(2)	90.2(4)
		O(4)–Re(2)–O(5)	86.5(4)
		O(6)–Re(2)–O(5)	81.3(4)
		N(2)–Re(2)–O(5)	89.8(4)
		O(4)–Re(2)–S(2)	99.6(3)
		O(6)–Re(2)–S(2)	93.1(3)
		N(2)–Re(2)–S(2)	84.9(3)
		O(5)–Re(2)–S(2)	172.2(3)
		O(4)–Re(2)–P(2)	89.4(3)
		O(6)–Re(2)–P(2)	86.4(3)
		N(2)–Re(2)–P(2)	174.7(3)
		O(5)–Re(2)–P(2)	93.6(3)
		S(2)–Re(2)–P(2)	91.3(1)

Table 3Selected bond lengths (Å) and angles (°) for [ReO(η^3 -OC₆H₄CH=NC₆H₄S)(η^2 -OC₆H₄C=NC₆H₄S)] (4)

Re(1)–O(1)	1.700(3)	O(1)–Re(1)–O(3)	167.52(15)
Re(1)–O(3)	1.989(3)	O(1)–Re(1)–N(1)	98.93(15)
Re(1)–N(1)	2.050(4)	O(3)–Re(1)–N(1)	86.03(14)
Re(1)–O(2)	2.076(3)	O(1)–Re(1)–O(2)	88.23(14)
Re(1)–N(2)	2.140(4)	O(3)–Re(1)–O(2)	80.04(13)
Re(1)–S(1)	2.3120(13)	N(1)–Re(1)–O(2)	93.02(14)
		O(1)–Re(1)–N(2)	93.30(15)
		O(3)–Re(1)–N(2)	81.30(13)
		N(1)–Re(1)–N(2)	167.29(15)
		O(2)–Re(1)–N(2)	83.86(13)
		O(1)–Re(1)–S(1)	102.16(12)
		O(3)–Re(1)–S(1)	89.67(10)
		N(1)–Re(1)–S(1)	84.37(12)
		O(2)–Re(1)–S(1)	169.55(9)
		N(2)–Re(1)–S(1)	96.48(11)