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Schiff base chemistry of the rhenium(V)-oxo core with ‘3+2’ ligand donor sets

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Abstract

Reactions of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with the bidentate ligands 2-(2-hydroxyphenyl) benzoxazole and (2'-hydroxyphenyl)-2-thiazoline resulted in the isolation of the complexes $[\text{ReOCl}_2(\text{OC}_6\text{H}_4\text{-2-C=NC}_6\text{H}_4\text{-2-O})(\text{PPh}_3)]$ (**1**) and $[\text{ReOCl}_2(\text{OC}_6\text{H}_4\text{-2-C=NCH}_2\text{CH}_2\text{S})(\text{PPh}_3)]$ (**2**). Reactions of **1** with the tridentate Schiff base ligands salicylaldehyde 2-hydroxyanil (H_2L^{1b}), salicylaldehyde 2-mercaptoanil (H_2L^{2b}) and *S*-benzyl-2-[(2-hydroxyphenyl)methylene] dithiocarbamate (H_2L^{3b}) yielded the ‘3+2’ rhenium(V) oxo species $[\text{ReO}(\text{OC}_6\text{H}_4\text{-2-C=NC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{O})]$ (**3**), $[\text{ReO}(\text{OC}_6\text{H}_4\text{-2-C=NC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{S})]$ (**4**) and $[\text{ReO}(\text{OC}_6\text{H}_4\text{-2-C=NC}_6\text{H}_4\text{O})\{\text{OC}_6\text{H}_4\text{CH=N-N=C}(\text{SCH}_2\text{C}_6\text{H}_5)\text{S}\}]$ (**5**). Similarly, the reactions of $[\text{ReOCl}_2(\text{OC}_6\text{H}_4\text{-2-C=NC}_6\text{H}_4\text{S})(\text{PPh}_3)]$ (**2**) with H_2L^{2b} , H_2L^{3b} and 2-[(2-hydroxyphenyl) methylene]-*N*-phenylhydrazinecarbothioamide (H_2L^{4b}) were exploited to prepare $[\text{ReO}(\text{OC}_6\text{H}_4\text{-2-C=NC}_6\text{H}_4\text{S})(\text{OC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{O})]$ (**6**), $[\text{ReO}(\text{OC}_6\text{H}_4\text{C=NC}_6\text{H}_4\text{S})\{\text{OC}_6\text{H}_4\text{CH=N-N=C}(\text{SCH}_2\text{C}_6\text{H}_5)\text{S}\}]$ (**7**) and $[\text{ReO}(\text{OC}_6\text{H}_4\text{-2-C=NC}_6\text{H}_4\text{S})\{\text{OC}_6\text{H}_4\text{CH=N-N=C}(\text{NHC}_6\text{H}_5)\}]$ (**8**), respectively.

Keywords

Oxorhenium complexes; Schiff base complexes; Crystal structures; ‘3+2’ Rhenium(V) chemistry

1. Introduction

The continued expansion of the chemistry of technetium and rhenium reflects the applications of the radionuclides of these elements to diagnostic and therapeutic nuclear medicine, respectively [1]. The Group VII congeners, technetium and rhenium, exhibit considerable chemical diversity, with complexes of oxidation states –1 to +7 having been reported. This chemical versatility is reflected in a number of robust chemical cores which have been investigated for potential applications to radiopharmaceutical development. These include the metal(V)-oxo $\{\text{MO}\}^{3+}$ [1], the metal(V)-nitrido $\{\text{MN}\}^{2+}$ [2–4], the metal(V)-imido $\{\text{MNR}\}^{3+}$ [5–8], the metal(III)-hydrazino $\{\text{M}(\text{NNR})\}^{x+}$ [9,10] and the metal(I)-tricarbonyl $\{\text{M}(\text{CO})_3\}^+$ [11–15] cores. The most extensively developed chemistry is that of the technetium and rhenium complexes of the metal(V)-oxo core [1]. While a major class of technetium and rhenium complexes are represented by the tetradentate $[\text{N}_x\text{S}_{(4-x)}]$ oxometal(V) compounds, another successful approach to the development of radiopharmaceuticals of technetium and rhenium has exploited Schiff base ligands to stabilize the $[\text{MO}]^{3+}$ core [16–32].

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In chemistry paralleling that of the $\{\text{MO}\}^{3+}$ core with tetradentate aminothiols ligand types $[\text{N}_x\text{S}_{(4-x)}]$, polydentate Schiff base ligands derived from salicylaldehyde and diamines (salenes) affording $[\text{O}_2\text{N}_2]$ donor sets have been extensively studied. However, the evolution of the chemistry of the $\{\text{MO}\}^{3+}$ core by Spies and others demonstrated that mononuclear, neutral and low molecular weight technetium and rhenium complexes of the general type $[\text{MO}(\text{SXS})(\text{SR})]$ were readily attainable by the reaction of tridentate dithiol ligands HSXS ($\text{X}=\text{S}, \text{O}, \text{NR}$) and monodentate thiol ligand R-SH with starting materials containing the $\{\text{MO}\}^{3+}$ [$\text{M}=\text{Tc}, \text{Re}$] core [33–37]. Using this approach, $\text{Tc}(\text{V})$ and $\text{Re}(\text{V})$ compounds based on the ‘3+1’ donor ligand design based on tridentate Schiff bases in combination with monothiols have also been prepared [25,28].

Not unexpectedly, these ‘3+1’ complexes are found to be relatively unstable in vitro and in vivo due to the metabolism and substitution of the labile monodentate ligand through transchelation by physiological thiols such as cysteine and glutathione [38], leading to a accumulation of the products in thiolate-rich organs such as the liver, rather than localization in the organs of interest. One approach to the preparation of more stable 18 electron structures, in contrast to the 16 electron structures of the ‘3+1’ $\{\text{MO}\}^{3+}$ complexes, is to expand the coordination sphere at the technetium or rhenium site by exploiting ‘3+2’ ligand chemistry, which disposes a tridentate and a bidentate ligand set about the oxometal core [39–41].

We previously demonstrated that ‘3+2’ six coordinate oxorhenium complexes were readily accessible with a bidentate ligand such as 8-hydroxy-5-nitroquinoline and a variety of tridentate (ONS) and (ONO) donor ligands, including the Schiff bases $\text{HOC}_6\text{H}_4\text{-2-CH=NC}_6\text{H}_4\text{XH}$ ($\text{X}=\text{O}, \text{S}$), that is salicylaldehyde-2-hydroxyanil (H_2L^{1b}) and salicylaldehyde-2-mercaptoanil (H_2L^{2b}), respectively [42]. As an extension of these studies, we have prepared a series of ‘3 + 2’ complexes of the $\{\text{ReO}\}^{3+}$ core by reacting $[\text{ReOCl}_2(\text{L}^{1a})(\text{PPh}_3)]$ (**1**) and $[\text{ReOCl}_2(\text{L}^{2a})(\text{PPh}_3)]$ (**2**), where HL^{1a} is 2-(2-hydroxyphenyl)benzoxazolate and HL^{2a} is (2'-hydroxy-phenyl)-2-thioazoline, with the series of tridentate Schiff base ligands salicylaldehyde-2-hydroxyanil (H_2L^{1b}), salicylaldehyde-2-mercaptoanil (H_2L^{2b}), *S*-benzyl-2-[(2-hydroxyphenyl)methylene]dithiocarbamate (H_2L^{3b}), and 2-[(2-hydroxyphenyl)methylene]-*N*-phenyl-hydrazinecarbothioamide (H_2L^{4b}) (Scheme 1). The structures of $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{-2-CH=NC}_6\text{H}_4\text{-2-O})-(\eta^2\text{-OC}_6\text{H}_4\text{C=NC}_6\text{H}_4\text{-2-O})]$ (**3**), $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{-2-CH=NC}_6\text{H}_4\text{-2-S})(\eta^2\text{-OC}_6\text{H}_4\text{C=NC}_6\text{H}_4\text{-2-O})]\cdot\text{MeOH}$ (**4-MeOH**), $[\text{ReO}\{\eta^3\text{-OC}_6\text{H}_4\text{-2-CH=N-N=C}(\text{SCH}_2\text{C}_6\text{H}_5)\text{-S}\}(\eta^2\text{-OC}_6\text{H}_4\text{C=NC}_6\text{H}_4\text{-2-O})]\cdot\text{CH}_2\text{Cl}_2$ (**5-CH}_2\text{Cl}_2**) and $[\text{ReO}(\eta^3\text{-OC}_6\text{H}_4\text{-2-CH=NC}_6\text{H}_4\text{-2-O})(\eta^2\text{-OC}_6\text{H}_4\text{C=NC}_6\text{H}_4\text{-2-S})]$ (**6**) are reported.

2. Experimental

2. 1. General considerations

^1H 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 Paragon 1000 FTIR. Elemental analysis for carbon, hydrogen and nitrogen were carried out by Oneida Research Services, Whitesboro, NY. All chemicals were of reagent grade and were used without further purification. All reactions were performed under a nitrogen atmosphere. $[\text{ReOCl}_3(\text{PPh}_3)_2]$ was prepared according to literature [43]. Bidentate ligands 2-(2-hydroxyphenyl)benzoxazolate (HL^{1a}) [44] and (2'-hydroxyphenyl)-2-thiazoline (HL^{2a}) [45]; tridentate Schiff base ligands salicylaldehyde 2-hydroxyanil (H_2L^{1b}) [46], salicylaldehyde 2-mercaptoanil (H_2L^{2b}) [47], *S*-benzyl-2-[(2-hydroxyphenyl)methylene]dithiocarbamate (H_2L^{3b}) [48], and 2-[(2-hydroxyphenyl)methylene]-*N*-phenyl-hydrazinecarbothioamide (H_2L^{4b}) [49] were prepared according to literature method with minor modifications.

2. 2. Synthesis

2.2.1. General procedure for the synthesis of intermediate complexes

[ReOCl₂(L^{ma})(PPh₃)]—To a refluxing solution of [ReOCl₃(PPh₃)₂] (200 mg, 0.24 mmol) in chloroform (50 cm³) was added with stirring 2-(2-hydroxyphenyl)benzoxazolate (HL^{1a}) or (2'-hydroxyphenyl)-2-thiazoline (HL^{2a}) (0.24 mmol) in chloroform (20 cm³). The olive green reaction mixture was refluxed for 40 min, while the color changed gradually to emerald green. The reaction mixture was cooled down and evaporated under reduced pressure to give a green solid residue, which was triturated with ethanol (30 cm³) to give the desired intermediate complex.

2.2.1.1. [ReOCl₂(η²-OC₆H₄-2-C = NC₆H₄-2-O)(PPh₃)] (1): Yield: 136 mg, 76%. *Anal.* Calc. for C₃₁H₂₃Cl₂-NO₃Pre: C, 49.9; H, 3.09; N, 1.88. Found: C, 50.3; H, 3.14; N, 1.94%.

2.2.1.2. [ReOCl₂(η²-OC₆H₄-2-C = NCH₂CH₂S)(PPh₃)] (2): Yield: 118. mg, 69%. *Anal.* Calc. for C₂₇H₂₃Cl₂-NO₂PSRe: C, 45.4; H, 3.23; N, 1.96. Found: C, 45.6; H, 3.14; N, 2.01%.

2.2.2. General procedure for the synthesis of the '3+2' complexes [ReO(η²-L^{ma})(η³-L^{mb})]

—To a refluxing solution of [ReOCl₂(η²-L^{ma})(PPh₃)] (0.05 mmol) in 1:1 CHCl₃ + CH₃OH (30 cm³) was added the appropriate tridentate ligand (0.05 mmol) with stirring. Four drops of triethylamine were then added and the solution was refluxed for additional 30 min, after which the color of the reaction mixture turned from emerald green to brownish red. The solvent was evaporated under reduced pressure and the dark red solid residue was redissolved in methylene chloride (50 cm³) and washed with water. The organic layer was separated from the mixture and dried over Na₂SO₄. The volume was reduced to 3 cm³ and then purified on silica gel column using gradient solvent (from 100% CHCl₃ to 90:10 CHCl₃: acetone).

2.2.2.1. [ReO(η³-OC₆H₄-2-CH=NC₆H₄-2-O)(η²-OC₆H₄-2-O)] · [ReO(η²-L^{1b})(η²-L^{1a})] (3): Yield: 22 mg, 71%. Slow evaporation of pentane into complex **3** in minimum amount of CH₂Cl₂ afforded red plates suitable for X-ray analysis. FT-IR (cm⁻¹, KBr pellet): 1597, 1530, 966. ¹H NMR (CDCl₃, ppm): 8.95 (s, 1H, CH=N), 7.96 (dd, 1H, *J*₁ = 8.1 Hz, *J*₂ = 1.5 Hz, ArH), 7.79 (d, 1H, *J* = 8.4 Hz, ArH), 7.70 (dd, 1H, *J*₁ = 6.6 Hz, *J*₂ = 1.8 Hz, ArH), 7.55–7.45 (m, 2H, ArH), 7.41 (dd, 1H, *J*₁ = 7.8 Hz, *J*₂ = 1.2 Hz, ArH), 7.35–7.1 (m, 3H, ArH), 7.04 (d, 1H, *J* = 8.1 Hz, ArH), 7.0–6.85 (m, 2H, ArH), 6.75–6.65 (m, 2H, ArH), 6.61 (d, 1H, *J* = 7.8 Hz, ArH). *Anal.* Calc. for C₂₆H₁₇N₂O₅Re: C, 50.1; H, 2.73; N, 4.49. Found: C, 49.9; H, 2.82; N, 4.38%.

2.2.2.2. [ReO(η³-OC₆H₄-2-CH=NC₆H₄-2-S)(η²-OC₆H₄-2-O)] · MeOH, [ReO(η²-L^{2b})(η²-L^{1a})] · MeOH (4): Yield: 25 mg, 76%. X-ray quality crystals were obtained by slow evaporation from a CH₂Cl₂-MeOH mixture. FT-IR (cm⁻¹, KBr pellet): 1600, 1530, 965. ¹H NMR (CDCl₃, ppm): 8.86 (s, 1H, CH=N), 7.73 (d, 1H, *J* = 8.1 Hz, ArH), 7.47 (dd, 1H, *J*₁ = 7.8 Hz, *J*₂ = 1.8 Hz, ArH), 7.4–7.3 (m, 4H, ArH), 7.17 (t, 2H, *J* = 7.2 Hz, ArH), 6.9–6.8 (m, 2H, ArH), 6.75–6.65 (m, 2H, ArH), 6.50 (d, 1H, *J* = 8.4 Hz, ArH), 6.75–6.65 (m, 2H, ArH), 6.61 (d, 1H, *J* = 7.8 Hz, ArH). *Anal.* Calc. for C₂₇H₂₁N₂O₅SRe: C, 48.3; H, 3.13; N, 4.17. Found: C, 48.2; H, 3.08; N, 4.28%.

2.2.2.3. [ReO(η³-OC₆H₄-2-CH=N-N=C(SCH₂C₆H₅)-S)(η²-OC₆H₄-2-O)] · CH₂Cl₂, [ReO(η²-L^{3b})(η²-L^{1a})] · CH₂Cl₂ (5): Yield: 22 mg, 71%. X-ray quality crystals were grown by slow evaporation from a CH₂Cl₂/MeOH mixture. FT-IR (cm⁻¹, KBr pellet): 1579, 1540, 963. ¹H NMR (CDCl₃, ppm): 9.17 (s, 1H, CH₃N), 8.0–7.9 (m, 2H, ArH), 7.7–7.1 (m, 10H, ArH), 7.0–6.85 (m, 2H, ArH), 7.0–6.85 (m, 2H, ArH), 6.60 (t, 1H, *J* = 8.4 Hz,

ArH), 6.51 (d, 1H, $J = 7.5$ Hz, ArH), 6.42 (d, 1H, $J = 7.5$ Hz, ArH), 4.61 (s, 2H, CH₂). *Anal.* Calc. for C₂₉H₂₂Cl₂N₃O₄S₂Re: C, 43.7; H, 2.76; N, 5.27. Found: C, 43.5; H, 2.82; N, 5.36%.

2.2.2.4. [ReO(η³-OC₆H₄-2-CH=NC₆H₄-2-O)(η²-OC₆H₄C=NCH₂CH₂-S)], [ReO(η²-L^{2b})(η²-L^{2a})] (6): Yield: 18 mg, 62%. Slow evaporation of ethyl ether into complex **6** in minimum amount of CH₂Cl₂ afforded red plates suitable for X-ray analysis. FT-IR (cm⁻¹, KBr pellet): 1607, 1542, 962. ¹H NMR (CDCl₃, ppm): 8.95 (s, 1H, CH=N), 7.75 (d, 1H, $J = 6.9$ Hz, ArH), 7.67 (dd, 1H, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, ArH), 7.32 (t, 2H, $J = 6.9$ Hz, ArH), 7.2–7.1 (m, 2H, ArH), 6.98 (t, 1H, $J = 9$ Hz, ArH), 6.82 (t, 1H, $J = 7.5$ Hz, ArH), 6.52, (t, 1H, $J = 6.9$ Hz, ArH), 6.29 (t, 2H, $J = 8.7$ Hz, ArH), 4.88 (m, 1H, CH₂), 4.59 (m, 1H, CH₂), 3.85 (m, 1H, CH₂), 3.63 (m, 1H, CH₂). *Anal.* Calc. for C₂₂H₁₇N₂O₄SRe: C, 44.7; H, 2.88; N, 4.74. Found: C, 44.8; H, 2.81; N, 4.86%.

2.2.2.5. [ReO(η³-OC₆H₄-2-CH=N-N=C(SCH₂C₆H₅)-S)(η²-OC₆H₄C=NCH₂CH₂-S)], [ReO(η²-L^{3b})(η²-L^{2a})] (7): Yield: 19 mg, 64%. FT-IR (cm⁻¹, KBr pellet): 1604, 1582, 967. ¹H NMR (CDCl₃, ppm): 9.14 (s, 1H, CH=N), 7.55–7.2 (m, 8H, ArH), 7.12 (t, 1H, $J = 7.8$ Hz, ArH), 6.7–6.6 (m, 2H, ArH), 6.41 (d, 1H, $J = 8.4$ Hz, ArH), 5.0–4.85 (m, 1H, CH₂), 4.67 (s, 2H, CH₂Ph), 4.3–4.15 (m, 1H, CH₂), 3.79 (tt, 1H, $J = 10.2$ Hz, CH₂), 3.7–3.6 (m, 1H, CH₂). *Anal.* Calc. for C₂₄H₂₀-N₃O₃S₂Re: C, 44.4; H, 3.08; N, 6.47. Found: C, 44.6; H, 2.99; N, 6.59%.

2.2.2.6. [ReO(η³-OC₆H₄-2-CH=N-N=C(NHC₆H₅)-S)(η²-OC₆H₄C=NCH₂CH₂-S)], [ReO(η²-L^{4b})(η²-L^{2a})] (8): Yield: 17 mg, 53%. FT-IR (cm⁻¹, KBr pellet): 1599, 1529, 968. ¹H NMR (CDCl₃, ppm): 9.09 (s, 1H, CH=N), 7.70 (d, 1H, $J = 7.8$ Hz, ArH), 7.53 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, ArH), 7.45–7.05 (m, 7H, ArH), 6.82 (t, 1H, $J = 7.8$ Hz, ArH), 6.67 (d, 2H, $J = 7.8$ Hz, ArH), 6.44 (d, 1H, $J = 8.4$ Hz, ArH), 5.05–4.9 (m, 1H, CH₂), 4.75–4.6 (m, 1H, CH₂), 4.35–4.2 (m, 1H, CH₂), 4.25–4.1 (m, 1H, CH₂). *Anal.* Calc. for C₂₃H₁₉N₄O₃S₂Re: C, 42.5; H, 2.93; N, 8.63. Found: C, 42.0; H, 2.89; N, 8.88%.

2.3. X-ray crystallography

The selected crystals of **3–6** were measured with a Bruker P4 diffractometer equipped with the SMART CCD system [50] and using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data collection was carried out at 89(5) K. The data were corrected for Lorentz and polarization effects, and absorption corrections were made using SADABS [51]. Neutral atom scattering factors were taken from Cromer and Waber [52]. And anomalous dispersion corrections were taken from those of Creagh and McAuley [53]. All calculations were performed using SHELXL [54]. The structures were solved by direct methods [55] 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 $\Delta/\sigma_{\max}$ 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 $\Delta/\sigma_{\max}$ was again less than 0.001. No anomalies were encountered in the refinements. The relevant parameters for crystal data, data collection, structure solution and refinement are summarized in Table 1, and important bond lengths and angles in Tables 2–5.

3. Results and discussion

The bidentate ligand 2-(2-hydroxyphenyl)benzoxazole (HL^{1a}) was prepared from the condensation reaction of 2-cyanophenol and 2-aminophenol as shown in Scheme 2. The

analogous bidentate ligand (2'-hydroxyphenyl)-2-thiazoline (HL^{2a}) was isolated in a similar fashion in the reaction of 2-cyanophenol and 2-mercaptoethylalcohol. The tridentate Schiff bases salicylaldehyde-2-hydroxyanil (H₂L^{1b}) and salicylaldehyde-2-mercaptoanil (H₂L^{2b}) were synthesized in the reactions of 2-hydroxybenzaldehyde with 2-aminophenol and 2-aminothiophenol, respectively (Scheme 3). *S*-benzyl-2-[(2-hydroxyphenyl)methylene]dithiocarbazate (H₂L^{3b}) was prepared by condensation of salicylaldehyde with *S*-benzylthiocarbazate in ethanol solution. The tridentate Schiff base ligand 2-[(2-hydroxyphenyl)methylene]-*N*-phenyl-hydrazinecarbothioamide (H₂L^{4b}) was synthesized by reacting salicylaldehyde with 4-phenyl-3-thiosemicarbazide.

The '3+2' type complexes were prepared in a two step synthesis. The Re(V)-oxo precursor [ReOCl₃-(PPh₃)₂] was reacted with H₂L^{1a} or H₂L^{2a} to give the intermediate complexes [ReOCl₂(L^{1a})(PPh₃)] (**1**) and [ReOCl₂(L^{2a})(PPh₃)] (**2**), respectively (Eq. (1)). Subsequent reactions of **1** and **2** with the appropriate tridentate Schiff base ligands yielded the '3+2' complexes of the {ReO}³⁺ core (Eq. (2)).

The '3+2' complexes **3–8** invariably exhibit a strong band in the infrared spectrum at 960–968 cm⁻¹ attributed to ν(Re=O). The remainder of the spectra were dominated by ν(C=C) stretching between 1400 and 1600 cm⁻¹ and ν(C=N) stretching ranging from 1600 to 1610 cm⁻¹.

The ¹H NMR spectra displayed resonances characteristic of aromatic protons from approximately 6.85 to 8.15 ppm. The spectra of **3–8** also featured a singlet at approximately 9.00 to 9.15 ppm associated with the imine proton of the tridentate Schiff base ligand.

The Schiff base ligands H₂L^{3b} and H₂L^{4b} may exist in both the thione (**A**) and thiolo (**B**) forms (Scheme 4). The thione group is relatively unstable and tends to convert to the more stable C–S bond by enolization, if there is at least one proton adjacent to the thione group [56]. We have previously noted that for the case of H₂L^{3b} the thione/thiol tautomers are present in approximately 77/23 ratio based on the integration of the {CH=N} imine proton [30]. On metal complexation in **5** and **7** of {L^{3b}}²⁻ and in **8** of {L^{4b}}²⁻, the ligands are found in the dianionic forms, involving deprotonation of the phenolic and thiolate SH groups. This is apparent from the disappearance of the ν(OH) (3110 cm⁻¹) and ν(NH) (2970–2980 cm⁻¹), as well as the absence of ν(SH) or ν(C=S) vibrations in the infrared spectra of **5**, **7** and **8** [57]. The [ONS] mode of chelation through phenolic oxygen, azomethine nitrogen and sulfur thiol of **B** is confirmed from the red-shift (15–20 cm⁻¹) of the ν(C=N) [58] and blue shift (30–40 cm⁻¹) of the ν(C–O) vibrations of the parent ligands [59]. Furthermore, in the ¹H NMR spectra of **5**, **7** and **8**, the phenolic proton resonance of the free ligand disappears and the azomethine proton signals are shifted downfield [60].

As shown in Fig. 1, the structure of **3** exhibits distorted octahedral geometry about the Re(V) center, defined by a terminal oxo-group, the oxygen and nitrogen donors of the {L^{1a}}¹⁻ ligand, and the two oxygen and nitrogen donors of the tridentate {L^{1b}}²⁻ Schiff base ligand. The [ONO] donors of the tridentate Schiff base adopt a meridional disposition about the Re(V) center; consequently, the donors occupy cisoid positions relative to the oxo-group. The [ON] donors of the bidentate (L^{1a})¹⁻ ligand occupy the remaining positions, with the N

donor in the equatorial plane with the [ONO] donors of the Schiff base. It is significant that the oxo-group of **3** does not exert an appreciable *trans* influence as indicated by the Re–O4 distance of 2.013(6) Å, compared to Re–O2 and Re–O3 distances of 2.029(8) and 2.011(7) Å, respectively. As shown by the data summarized in Table 6, this appears to be a characteristic feature of the structures of ‘3+2’ complexes of the {ReO}³⁺ core.

The structure of **4**, shown in Fig. 2, is analogous to that of **3**. Once again, the [ONS] donors of the tridentate Schiff base ligand occupy meridional positions *cis* to the terminal oxo-group. The oxygen donor of the bidentate ligand is *trans* to the oxo-group, and the nitrogen donor occupies the fourth positions of the equatorial plane. In this case also, there is no evident *trans* influence of the terminal oxo-group.

The structure of **5**, shown in Fig. 3, again features the [ONS] donors of the tridentate Schiff base ligand occupying meridional positions *cis* to the terminal oxo-group. The oxygen donor of the bidentate ligand is *trans* to the oxo-group, while the nitrogen donor completes the bonding in the equatorial plane. There is no apparent *trans* influence associated with the terminal oxo-group.

As shown in Fig. 4, the structure of **6** is analogous to that of **3** with the ligand {L^{2a}}¹⁻ replacing the bidentate {L^{1a}}¹⁻ of **3**. The metrical parameters are unexceptional.

In all cases, the N1–C7 distance (1.27(1)–1.31(1) Å) and the valence angles at N1 (114.6(7)–123.4(8)°) confirm that the N1 site is sp² hybridized and the ligand is in the Schiff base form. Similarly, the N2–C2 bond lengths (1.28(2)–1.32(1) Å) and the N2 valence angles (106.3(8)–128.3(4)°) in **3**, **4**, and **6** and the N3–C27 bond length (1.32(1) Å) and the N3 valence angles (107.6(5)–126.3(6)°) in **5** are consistent with C–N double bond character and sp² hybridization at the N2 site in **3**, **4** and **6** and at the N3 site in **5**. This observation confirms that the bidentate ligands in **3**, **4** and **6** adopt the oxidized 2-(2-hydroxyphenyl)benzoxazolate form, while that in **5** is in the (2-hydroxyphenyl)-2-thiazolate form.

4. Conclusions

The ‘3+2’ chemistry of the {ReO}³⁺ core is readily accessed by exploiting tridentate Schiff base ligands. Thus, a variety of Schiff base complexes with [ONO] or [ONS] donor sets react smoothly with [ReOCl(η²-L^{ma})(PPh₃)] complexes **1** and **2** to provide a series of ‘3+2’ compounds of the general type [ReO(η²-L^{ma})(η³-L^{mb})] (**4–8**). These results confirm that the Schiff base chemistry of the {ReO}³⁺ core may be exploited in the elaboration of materials whose size, shape, molecular weight, charge and lipophilicity may be systematically varied.

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Fig. 1.
A view of the structure of **3**, showing the atom labeling scheme.

Fig. 2.
A view of the structure of **4**.

Fig. 3.
A view of the structure of **5**.

Fig. 4.
A view of the structure of **6**.

Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Table 1

Summary of crystal data for the structures of [ReO(η^3 -OC₆H₄-2-CH=NC₆H₄-2-O) (η^2 -OC₆H₄C=NC₆H₄-2-O)] (**3**), [ReO(η^3 -OC₆H₄-2-CH=NC₆H₄-2-S)(η^2 -C₆H₄C=NC₆H₄-2-O)] · MeOH (**4**·MeOH), [ReO(η^3 -OC₆H₄-2-CH=N-N=C(SCH₂C₆H₅)S)(η^2 -OC₆H₄C=NC₆H₄-2-O)] · CH₂Cl₂ (**5**·CH₂Cl₂) and [ReO(η^3 -OC₆H₄-2-CH=NC₆H₄-2-O)(η^2 -OC₆H₄C=NCH₂CH₂S)] (**6**)

	3	4·MeOH	5·CH₂Cl₂	6
Empirical formula	C ₂₆ H ₁₇ N ₂ O ₅ Re	C ₂₇ H ₂₁ N ₂ O ₅ Re	C ₂₉ H ₂₂ Cl ₂ N ₃ O ₄ S ₂ Re	C ₂₂ H ₁₇ O ₄ N ₂ ReS
Formula weight	623.62	671.72	797.72	591.64
Crystal size (mm ³)	0.15 × 0.13 × 0.10	0.40 × 0.20 × 0.05	0.25 × 0.20 × 0.15	0.20 × 0.20 × 0.15
Crystal system	monoclinic	orthorhombic	triclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> (Å)	9.589(1)	12.605(2)	8.664(1)	7.126(1)
<i>b</i> (Å)	25.719(4)	16.455(2)	12.493(2)	22.406(3)
<i>c</i> (Å)	9.573(1)	22.567(3)	13.461(2)	24.624(4)
α (°)	90	90	78.214(2)	90
β (°)	115.012(2)	90	87.953(2)	90
γ (°)	90	90	74.632(2)	90
<i>V</i> (Å ³)	2139.3(5)	4680.9(11)	1374.9(3)	3931.7(10)
<i>Z</i>	4	8	2	8
<i>D</i> _{calc} (g cm ⁻³)	1.936	1.906	1.923	1.999
<i>F</i> (000)	1208	2624	780	2288
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	5.724	5.325	4.808	6.321
θ range (°)	1.58–28.31	1.80–28.42	1.55–28.31	1.65–28.30
No. of unique data	5132	5738	6363	4843
Parameters refined	307	327	370	272
<i>R</i> ₁ (<i>wR</i> ₂)	0.0574(0.1059)	0.0610(0.1365)	0.0532(0.1012)	0.0574(0.0991)
Goodness-of-fit, <i>S</i> (<i>F</i> ²)	0.962	1.058	0.911	0.959

Table 2Selected bond lengths (Å) and bond angles (°) for **3**

<i>Bond lengths</i>			
Re(1)–O(1)	1.689(6)	Re(1)–N(2)	2.119(8)
Re(1)–O(3)	2.011(7)	N(1)–C(7)	1.270(13)
Re(1)–O(4)	2.013(6)	N(1)–C(8)	1.428(13)
Re(1)–O(2)	2.029(8)	N(2)–C(20)	1.301(12)
Re(1)–N(1)	2.058(10)	N(2)–C(21)	1.401(12)
<i>Bond angles</i>			
O(1)–Re(1)–O(3)	102.0(3)	O(3)–Re(1)–N(2)	91.2(3)
O(1)–Re(1)–O(4)	170.3(3)	O(4)–Re(1)–N(2)	82.1(3)
O(3)–Re(1)–O(4)	84.9(3)	O(2)–Re(1)–N(2)	92.7(3)
O(1)–Re(1)–O(2)	92.0(3)	N(1)–Re(1)–N(2)	166.3(3)
O(3)–Re(1)–O(2)	165.4(3)	C(7)–N(1)–C(8)	123.2(11)
O(4)–Re(1)–O(2)	81.7(3)	C(7)–N(1)–Re(1)	121.9(8)
O(1)–Re(1)–N(1)	101.3(3)	C(8)–N(1)–Re(1)	114.6(7)
O(3)–Re(1)–N(1)	80.2(3)	C(20)–N(2)–C(21)	106.3(8)
O(4)–Re(1)–N(1)	86.6(3)	C(20)–N(2)–Re(1)	125.7(7)
O(2)–Re(1)–N(1)	93.2(3)	C(21)–N(2)–Re(1)	128.0(6)
O(1)–Re(1)–N(2)	90.9(3)		

Table 3Selected bond lengths (Å) and bond angles (°) for **4**·MeOH

<i>Bond lengths</i>			
Re(1)–O(1)	1.701(6)	Re(1)–S(1)	2.306(2)
Re(1)–O(3)	2.032(6)	N(1)–C(7)	1.312(11)
Re(1)–N(1)	2.063(7)	N(1)–C(8)	1.442(10)
Re(1)–O(2)	2.080(6)	N(2)–C(20)	1.322(11)
Re(1)–N(2)	2.134(7)	N(2)–C(21)	1.420(11)
<i>Bond angles</i>			
O(1)–Re(1)–O(3)	167.4(3)	O(3)–Re(1)–S(1)	88.6(2)
O(1)–Re(1)–N(1)	99.5(3)	N(1)–Re(1)–S(1)	84.1(2)
O(3)–Re(1)–N(1)	87.5(3)	O(2)–Re(1)–S(1)	167.2(2)
O(1)–Re(1)–O(2)	90.4(3)	N(2)–Re(1)–S(1)	95.71(19)
O(3)–Re(1)–O(2)	78.8(2)	C(7)–N(1)–C(8)	121.0(7)
N(1)–Re(1)–O(2)	92.9(3)	C(7)–N(1)–Re(1)	121.4(6)
O(1)–Re(1)–N(2)	91.3(3)	C(8)–N(1)–Re(1)	117.4(6)
O(3)–Re(1)–N(2)	81.4(3)	C(20)–N(2)–C(21)	106.4(7)
N(1)–Re(1)–N(2)	169.0(3)	C(20)–N(2)–Re(1)	125.1(6)
O(2)–Re(1)–N(2)	84.8(2)	C(21)–N(2)–Re(1)	128.3(5)
O(1)–Re(1)–S(1)	102.4(2)		

Table 4Selected bond lengths (Å) and bond angles (°) for **5**·CH₂Cl₂

<i>Bond lengths</i>			
Re(1)–O(1)	1.693(6)	N(1)–C(7)	1.313(12)
Re(1)–O(3)	1.980(6)	N(1)–N(2)	1.421(10)
Re(1)–N(1)	2.031(8)	N(2)–C(8)	1.295(12)
Re(1)–O(2)	2.066(6)	N(3)–C(22)	1.315(12)
Re(1)–N(3)	2.166(8)	N(3)–C(23)	1.428(11)
Re(1)–S(1)	2.329(3)		
<i>Bond angles</i>			
O(1)–Re(1)–O(3)	166.8(3)	O(3)–Re(1)–S(1)	91.6(2)
O(1)–Re(1)–N(1)	98.4(3)	N(1)–Re(1)–S(1)	82.2(2)
O(3)–Re(1)–N(1)	90.0(3)	O(2)–Re(1)–S(1)	170.2(2)
O(1)–Re(1)–O(2)	89.4(3)	N(3)–Re(1)–S(1)	98.6(2)
O(3)–Re(1)–O(2)	80.1(3)	C(7)–N(1)–N(2)	113.4(8)
N(1)–Re(1)–O(2)	92.4(3)	C(7)–N(1)–Re(1)	124.0(7)
O(1)–Re(1)–N(3)	90.2(3)	N(2)–N(1)–Re(1)	122.6(6)
O(3)–Re(1)–N(3)	81.0(3)	C(8)–N(2)–N(1)	112.8(8)
N(1)–Re(1)–N(3)	171.0(3)	C(22)–N(3)–C(23)	107.6(8)
O(2)–Re(1)–N(3)	85.4(3)	C(22)–N(3)–Re(1)	126.3(6)
O(1)–Re(1)–S(1)	99.5(2)	C(23)–N(3)–Re(1)	125.9(6)

Table 5Selected bond lengths (Å) and bond angles (°) for **6**

<i>Bond lengths</i>			
Re(1)–O(1)	1.696(6)	Re(1)–N(1)	2.026(11)
Re(1)–O(3)	1.991(7)	Re(1)–O(2)	2.035(6)
Re(1)–O(4)	1.998(6)	Re(1)–N(2)	2.093(8)
<i>Bond angles</i>			
O(1)–Re(1)–O(3)	102.8(3)	O(4)–Re(1)–O(2)	81.5(3)
O(1)–Re(1)–O(4)	171.6(3)	N(1)–Re(1)–O(2)	90.7(7)
O(3)–Re(1)–O(4)	84.9(3)	O(1)–Re(1)–N(2)	94.6(3)
O(1)–Re(1)–N(1)	100.6(3)	O(3)–Re(1)–N(2)	89.1(3)
O(3)–Re(1)–N(1)	84.0(7)	O(4)–Re(1)–N(2)	82.0(3)
O(4)–Re(1)–N(1)	83.4(3)	N(1)–Re(1)–N(2)	164.3(4)
O(1)–Re(1)–O(2)	91.0(3)	O(2)–Re(1)–N(2)	92.7(3)
O(3)–Re(1)–O(2)	165.9(3)		

Table 6

Comparison of selected bond lengths (Å) for '3+2' Schiff base complexes of the [ReO]³⁺ core

Complex	η^2 -Ligand			η^3 -Ligand			Ref.
	Re=O	Re-O	Re-N	Re-O	Re-N	Re-S	
3	1.689(6)	2.013(6)	2.119(8), 2.011(7)	2.029(8)	2.058(10)		this work
4	1.701(6)	2.032(6)	2.134(7)	2.080(6)	2.063(7)	2.306(2)	this work
5	1.693(6)	1.980(6)	2.166(8)	2.066(6)	2.031(8)	2.329(3)	this work
6	1.696(6)	1.998(6)	2.093(8)	1.991(7)	2.026(11)	2.035(6)	this work
[ReO(η^3 -OC ₆ H ₄ CH=NC ₆ H ₄ -2-S)-(η^2 -OC ₆ H ₄ C=NC ₆ H ₄ -2-S)]	1.70(3)	1.989(3)	2.140(4)	2.076(3)	2.050(4)	2.312(1)	[32]
[ReO(η^2 -OC ₆ H ₄ C=NC ₆ H ₄ -2-S)] ³ ·OC ₆ H ₄ -2-CH=NC ₆ H ₄ C=NC ₆ H ₄ -2-S)] ² -8- <i>O</i> -5-NO ₂ -C ₉ H ₅ N)]	1.678(7)	2.052(7)	2.160(8)	1.990(8)	2.079(11)		[42]