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Preparation and Protonation Studies of *trans*-Dioxorhenium(V) Complexes with Imidazoles

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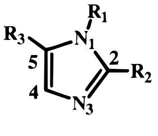
Reacting $ReO_2I(PPh_3)_2$ with imidazole (ImH) and its methylated derivatives 1-MeIm, 1,2-Me_2Im, 2-MeImH, and 4(5)-MeImH yielded salts of the *trans*-dioxo cation $[ReO_2L_4]^+$. Pure stable compounds were isolated for $X^- =$ I^- and L = ImH, 1,2-Me_2Im, and 1-MeIm and $X^- = B(C_6H_5)_4^-$ and L = 1-MeIm, 2-MeImH and 5-MeImH. The ν_{as}(O═Re═O) IR bands were observed between 765 and 794 cm^{-1}, whereas the ν_s Raman band appeared in the 900−925 cm^{-1} range. The compounds were also characterized by ^1H and ^{13}C NMR and UV−vis spectroscopies. Crystal structures were determined for three compounds: $[ReO_2(2\text{-MeImH})_4][B(C_6H_5)_4]\cdot 3CH_3OH$, triclinic, $P\bar{1}$, $a = 10.696(3)$ Å, $b = 15.128(4)$ Å, $c = 15.497(4)$ Å, $\alpha = 113.57(2)°$, $\beta = 97.25(2)°$, $\gamma = 95.94(2)°$, $Z = 2$, $R = 0.030$; $[ReO_2(1\text{-MeIm})_4][B(C_6H_5)_4]\cdot H_2O\cdot 0.5CH_3OH$, monoclinic, $P2_1/n$, $a = 15.619(2)$ Å, $b = 9.486(2)$ Å, $c = 27.387(4)$ Å, $\beta = 97.09(1)°$, $Z = 4$, $R = 0.057$; $[ReO_2(5\text{-MeImH})_4][B(C_6H_5)_4]$, orthorhombic, $P2_12_12_1$, $a = 10.199(2)$ Å, $b = 13.441(5)$ Å, $c = 28.798(10)$ Å, $Z = 4$, $R = 0.043$. The complexes adopt the *trans*-dioxo geometry, and the octahedra are remarkably regular. Protonation of $[ReO_2L_4]I$ was studied in methanol and in water. Acid dissociation constants were determined in aqueous solution for the $[ReO(OH)L_4]^{2+}$ (K_{a_1}) and $[ReO(OH_2)L_4]^{3+}$ (K_{a_2}) species of 1-MeIm ($pK_{a_1} = 2.0$, $pK_{a_2} = \sim -4.0$) and 1,2-Me_2Im ($pK_{a_1} = \sim 3.8$, $pK_{a_2} = \sim -4.1$). Iodide salts of $[ReO(OH)L_4]^{2+}$ were not stable enough to be isolated, but the $B(C_6H_5)_4^-$ salt of $[ReO(OH)(1,2\text{-Me}_2\text{Im})_4]^{2+}$ was obtained in pure form. The crystal structure of $[ReO(OH)(1,2\text{-Me}_2\text{Im})_4](I_3)_{0.5}(ReO_4)_{1.5}$ (monoclinic, $I2/a$, $a = 23.290(8)$ Å, $b = 10.863(7)$ Å, $c = 25.709(8)$ Å, $\beta = 94.36(3)°$, $Z = 8$, $R = 0.060$) showed the presence of octahedral dications in which the oxo and hydroxo groups are *trans* to one another and the Re−N bonds are displaced to the Re−OH side by the steric effect of the multiple Re−oxo bond. The σ-donor ability of imidazole, greater than that of pyridine, leads to more stable $[ReO_2L_4]^+$ compounds in which the Re═O double bond character is lower and the oxo groups are better nucleophiles.

Introduction

A decade ago, interesting spectroscopic properties were observed for $[ReO_2L_4]^+$ complexes (L = py or $^1/_2$ en) by Winkler and Gray,[1] who discussed promising applications for such systems in photophysics. In the meantime, several studies have been devoted to the photochemistry and electrochemistry of these systems.[2−4] Recently, related compounds attracted attention in connection with the utilization of the ^{186}Re and ^{188}Re nuclei for diagnostic purposes in radiopharmacy.[5]

The first report on *trans*-dioxo compounds of rhenium(V) with imidazoles appeared only recently,[6] despite the fact that Tc analogues had been known for some time.[7] Complexes were described for a few imidazole ligands, but the chloride salts isolated proved to be unstable: partial decomposition to perrhenate was frequent, and mixed $[ReO_2L_4]^+/[ReO(OH)L_4]^{2+}$ phases were isolated. In a preliminary spectroscopic study,[8] $[ReO_2(1\text{-MeIm})_4]^+$ exhibited absorption and luminescence properties comparable with those of the pyridine analogue,[1] but the emitting state was found to lie at higher energy and coupling of metal−ligand vibrations was detected in the vibronic structure. Efforts are being devoted to relate these peculiarities to structural and other features of these compounds, and for this reason, it appeared to be desirable to devise routes to pure and well-characterized salts. This paper describes the preparation of several *trans*-$[ReO_2L_4]^+$ salts with imidazole (ImH) and its 1-methyl (1-MeIm), 2-methyl (2-MeImH), 4-methyl (4(5)-MeImH),[9] and 1,2-dimethyl (1,2-Me_2Im) derivatives. The protonation of these species is also examined.



R_1	R_2	R_3	
H	H	H	**ImH**
CH_3	H	H	**1-MeIm**
H	CH_3	H	**2-MeImH**
H	H	CH_3	**5-MeImH**
CH_3	CH_3	H	**1,2-Me$_2$Im**

Experimental Section

Materials. Reactants were used as received from Aldrich ($KReO_4$, PPh_3, imidazoles, NH_4PF_6), Fisher ($NaBPh_4$), Johnson Matthey (HBF_4), or Anachemia (HI). Spectrograde acetone and methanol (American Chemicals or ACP Chemicals) and all other solvents (reagent grade) were used without further purification. Deuterated solvents were from Cambridge Isotope Laboratory or Aldrich.

Physical Measurements. Solution ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz spectrometer. ^1H spectra were referenced to the residual solvent signal (D_2O, δ 4.80; CD_3OD, δ 3.30;

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(1) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373. Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346.

(2) Ram, M. S.; Jones, L. M.; Ward, H. J.; Wong, Y. H.; Johnson, C. S.; Subramanian, P.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 2928.

(3) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256.

(4) Ram, M. S.; Johnson, C. S.; Blackbourn, R. L.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 238. Liu, W.; Welch, T. W.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 4044.

(5) Technetium and Rhenium in Chemistry and Nuclear Medicine; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; S. G. Editoriali: Padova, Italy 1995.

(6) Lebuis, A. M.; Young, J. M. C.; Beauchamp, A. L. *Can. J. Chem.* **1993**, *71*, 2070.

(7) Fackler, P. H.; Lindsay, M. J.; Clarke, M. J.; Kastner, M. E. *Inorg. Chim. Acta* **1985**, *109*, 39.

(8) Savoie, C.; Reber, C.; Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1995**, *34*, 3851.

(9) Conventional ring numbering starting with the N−H(R) position is used. The two tautomeric forms are designated as 4-MeImH (4-methyl-1*H*-imidazole) and 5-MeImH (5-methyl-1*H*-imidazole), respectively. The equilibrium mixture is represented by 4(5)-MeImH.

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dimethyl-d_6 sulfoxide (DMSO-d_6), δ 2.49 ppm) and converted to the conventional Me_4Si scale. ^{13}C spectra were recorded on the same instrument at 75.431 MHz. For solution spectra, dioxane was added to the D_2O samples as internal standard (δ 67.4 ppm). The CP-MAS spectra were referenced to the aromatic carbons of hexamethylbenzene (δ 132.1 ppm). Infrared spectra were recorded as CsI or KBr pellets on a Perkin-Elmer 783 spectrophotometer. The Raman spectra were recorded on a Jobin Yvon/ISA Mole S-3000 spectrophotometer, equipped with Spectra Physics Stabilite 2016 argon ion (514.5 nm) and Lexel 3500 krypton (647.1 nm) lasers. Electronic absorption spectra were obtained using a Varian/CARY-5E UV−vis−near-IR spectrophotometer. Elemental analyses were performed by Guelph Chemical Labs.

Preparation of $[ReO_2L_4]I$. The purple starting material $ReO_2I(PPh_3)_2$ was prepared by the literature method[10] using $KReO_4$ instead of $HReO_4$, as described by Brewer and Gray.[11] We found $ReO_2I(PPh_3)_2$ to be moderately sensitive to O_2, even in the solid state, decomposing to the dimer $[ReOI_2(PPh_3)_2(OReO_3)]$, as evidenced from the unit cell and ^{31}P NMR spectrum being identical with those obtained from an authentic sample.[12,13] The Re(V) starting material was therefore stored under argon, and all further manipulations involving this compound were carried out under controlled atmosphere. The $[ReO_2L_4]I$ salts were obtained by reacting $ReO_2I(PPh_3)_2$ with excess of the imidazole (L) in methanol.

$[ReO_2(1,2\text{-}Me_2Im)_4]I$. $ReO_2I(PPh_3)_2$ (1.17 g, 1.35 mmol) and 1,2-Me_2Im (2.64 g, 27.5 mmol) were stirred in methanol (10 mL). A light brown solution was obtained within 2 min and the mixture was refluxed for 20 min. After the dark brown solution was cooled to room temperature, toluene (10 mL) was added and the solvent was evaporated until the mother liquor lost its brown color. The mustard yellow powder was filtered and washed with toluene and diethyl ether; yield, 0.96 g (98%). IR (CsI, cm^{-1}): 790 (vs) ν_{as}(O═Re═O). Raman (cm^{-1}): 907 ν_s(O═Re═O). UV−vis (CH_3OH; λ, nm (ϵ, $M^{-1}\,cm^{-1}$)): 211 (3.2×10^4), 255 (6.2×10^3), 467 (3.5×10^2). UV−vis (H_2O; λ, nm (ϵ, $M^{-1}\,cm^{-1}$)): 194 (5.4×10^4), ∼223 (sh) (∼2.5×10^4), ∼255 (sh) (∼5×10^3), 480 (3.2×10^2). ^1H NMR (D_2O, ppm): δ 7.10 (d, H5), 6.78 (d, H4), 3.74 (s, N−CH_3), 2.28 (s, C−CH_3), ^3J(H4−H5) = 1.7 Hz. ^{13}C CP-MAS (ppm): δ 146.5 (C2), 130.6 (C4), 122.4 (C5), 33.3, and 32.0 (N−CH_3), 12.1 (C−CH_3). Anal. Calcd for $C_{20}H_{32}IN_8O_2Re$: C, 32.92; H, 4.42; I, 17.39; N, 15.36. Found: C, 32.86; H, 4.36; I, 17.15; N, 15.00.

$[ReO_2(1\text{-}MeIm)_4]I\cdot 2H_2O$. As above. IR (KBr, cm^{-1}): 793 (vs) ν_{as}(O═Re═O). Raman (cm^{-1}): 905 ν_s(O═Re═O). UV−vis (CH_3OH, nm): 211 (2.9×10^5), 265 (9.2×10^3), 473 (2.0×10^2). UV−vis (H_2O; λ, nm (ϵ, $M^{-1}\,cm^{-1}$)): 193 (6.3×10^4), 221 (2.5×10^4), 255 (9.2×10^3). ^1H NMR (D_2O; ppm): δ 7.65 (s, br, H2), 7.21 (t, H5), 7.00 (t, H4), 3.80 (s, N−CH_3), ^3J(H4−H5) ∼ ^4J(H2−H4) ∼ ^4J(H2−H5) ∼ 1.5 Hz. ^{13}C NMR (D_2O; ppm): δ 140.0 (C2), 129.5 (C4), 123.7 (C5), 35.0 (N−CH_3). ^{13}C CP-MAS (ppm; two nonequivalent ligands detected in the solid): δ 137.5, 135.9 (C2); 130.6, 128.9 (C4); 126.3, 122.3 (C5); 35.4, 34.2 (N−CH_3). Anal. Calcd for $C_{16}H_{28}IN_8O_4Re$: C, 27.08; H, 3.98; I, 17.89; N, 15.79. Found: C, 27.35; H, 3.70; I, 17.73; N, 16.00.

$[ReO_2(ImH)_4]I\cdot 2.5CH_3OH$. $ReO_2I(PPh_3)_2$ (2.39 g, 2.74 mmol) and imidazole (0.073 g, 11.7 mmol) were heated in methanol (25 mL) for 10 min. The brown solution was cooled to room temperature, and toluene (40 mL) was then added. The solution was evaporated, and the brick red oily residue was dried by pumping in vacuum. The sample was recrystallized in methanol; yield, 0.75 g (38%). IR (KBr; cm^{-1}): 780 (vs) ν_{as}(O═Re═O). UV−vis (CH_3OH; λ, nm (ϵ, $M^{-1}\,cm^{-1}$)): 221 (2.2×10^5), 258 (7.5×10^3), 474 (2.2×10^2). ^1H NMR (D_2O; ppm): δ 7.77 (t, H2), 7.29 (t, H5), 7.07 (t, H4), ^3J(H4−H5) ∼ ^4J(H2−H4) ∼ ^4J(H2−H5) ∼ 1.3 Hz. ^{13}C NMR (D_2O; ppm): δ 139.7 (C2), 128.8 (C4), 119.4 (C5). Anal. Calcd for $C_{14.5}H_{26}IN_8O_{6.5}Re$: C, 23.87; H, 3.59; I, 17.40; N, 15.36. Found: C, 24.00; H, 3.86; I, 17.53; N, 15.50. When excess ligand was used, the yield was improved, but the raw product contained an appreciable amount of free imidazole identified by NMR. Most of the free ligand could be removed by stirring in $CHCl_3$, filtering, and washing with CH_2Cl_2.

Preparation of $[ReO_2L_4][B(C_6H_5)_4]$. The salts were obtained by adding $Na[B(C_6H_5)_4]$ to the iodide generated *in situ* or isolated as described above. They are virtually insoluble in water, but somewhat soluble in methanol and acetone.

$[ReO_2(2\text{-}MeImH)_4][B(C_6H_5)_4]\cdot 2H_2O$. 2-MeImH (0.367 g, 4.470 mmol) was added to a suspension of $ReO_2I(PPh_3)_2$ (0.966 g, 1.11 mmol) in methanol (30 mL). The reaction mixture was heated for 35 min, after which time the greenish brown solution was allowed to cool. Excess toluene was added, and the solvent was evaporated until a dark brown oil (1 mL) was obtained. The iodide was not isolated as a solid, but an NMR spectrum run on the oily sample confirmed the presence of $[ReO_2(2\text{-}MeImH)_4]^+$. ^1H NMR (D_2O; ppm): δ 7.07 (d, H5), 6.78 (d, H4), 2.20 (s, N−CH_3), ^2J(H4−H5) = 1.8 Hz. The oil was diluted in methanol (5 mL) and $Na[B(C_6H_5)_4]$ (0.406 g, 1.186 mmol) was added to the solution. The solvent was allowed to evaporate slowly in open air, and the complex was isolated as a mustard yellow powder; yield, 0.954 g (95%). IR (CsI; cm^{-1}): 765 (sh) or 775 (vs) ν_{as}(O═Re═O) (interference from the $[B(C_6H_5)_4]^-$ band). Raman (cm^{-1}): 924 ν_s(O═Re═O). UV−vis (CH_3OH; λ, nm (ϵ, $M^{-1}\,cm^{-1}$)): 207 (8.7×10^5, this absorption band includes a strong $[B(C_6H_5)_4]^-$ component), 467 (2.1×10^2). ^1H NMR (CD_3OD; ppm): δ 2-MeImH, 7.10 (d, H5), 6.79 (d, H4), 2.27 (s, N−CH_3); $[B(C_6H_5)_4]^-$, 7.28 (m, 2H), 6.95 (t, 2H), 6.81 (t, 1H). Anal. Calcd for $C_{40}H_{48}BN_8O_4Re$: C, 53.27; H, 5.36; B, 1.19; N, 12.42. Found: C, 53.04; H, 5.24; B, 1.19; N, 12.42. Crystals suitable for X-ray diffraction were grown in methanol by slow evaporation. The recrystallized sample has the formula $[ReO_2(2\text{-}MeImH)_4][B(C_6H_5)_4]\cdot 3CH_3OH$.

$[ReO_2(1\text{-}MeIm)_4][B(C_6H_5)_4]$. $[ReO_2(1\text{-}MeIm)_4]I$ (0.232 g, 0.344 mmol) was dissolved in methanol (20 mL). $Na[B(C_6H_5)_4]$ was added in excess (0.297 g, 0.868 mmol) as a concentrated methanol solution. The solvent was allowed to partly evaporate, and a homogeneous brick-red crystalline solid precipitated; yield, 0.240 g (80%). Composition was determined from the X-ray diffraction work described below. IR (KBr; cm^{-1}): 794 (vs) ν_{as}(O═Re═O). ^1H NMR (CD_3OD; ppm): δ 1-MeIm, 7.73 (s, H2), 7.11 (d) and 7.10 (d) (H5/H4), 3.71 (s, N−CH_3) (^3J(H4−H5) ∼ ^4J(H2−H4) ∼ ^4J(H2−H5) ∼ 1.3 Hz); $[B(C_6H_5)_4]^-$, 7.26 (m, 2H), 6.93 (t, 2H), 6.80 (t, 1H).

$[ReO_2(5\text{-}MeImH)_4][B(C_6H_5)_4]$. Conversion to the tetraphenylborate salt was effected in methanol, as described for $[ReO_2(1\text{-}MeIm)_4][B(C_6H_5)_4]$, using 3 equiv of $Na[B(C_6H_5)_4]$. The crystals that grew out of the solution within 2 days were used for the crystal structure study; yield, 64%. IR (CsI; cm^{-1}): 775 (vs, br) ν_{as}(O═Re═O). ^1H NMR (CD_3OD; ppm): δ 5-MeImH, 7.59 (s, br, H2), ∼6.84 (H4, interference with anion signal), 2.20 (s, br, C-CH_3); $[B(C_6H_5)_4]^-$, 7.26 (m, 2H), 6.94 (t, 2H), 6.83 (t, 1H). Anal. Calcd for $C_{40}H_{44}BN_8O_2Re$: C, 55.49; H, 5.12; N, 12.94. Found: C, 55.42; H, 5.09; N, 12.76.

$[ReO(OH)L_4]^{2+}$ Iodides. In a typical run aimed at preparing $[ReO(OH)(ImH)_4](I)_2$, a methanol solution (0.22 M) of HI (4.5 mL, 0.99 mmol) was added to a suspension of $[ReO_2(ImH)_4]I$ (0.140 g, 0.227 mmol) in methanol (20 mL). The reaction mixture immediately took a purple color, and all of the solid eventually dissolved. After the mixture was stirred for 2 min, the solvent was evaporated to a residual volume of 1 mL, without formation of a precipitate. The purple complex was precipitated by adding excess diethyl ether, filtered and washed with diethyl ether. The presence of $[ReO(OH)(ImH)_4]^{2+}$ in the sample is deduced from the strong IR band at 957 cm^{-1} for ν(Re═O), whereas the strong ν_{as}(O═Re═O) band of $[ReO_2(ImH)_4]^+$ at ∼780 cm^{-1} is absent. The species remains $[ReO(OH)(ImH)_4]^{2+}$ in DMSO, as evidenced from the violet color of the solution. The ^1H NMR resonances (DMSO-d_6) at relatively high field (7.95 (H2), 7.46 (H5), and 6.96 ppm (H4)) are consistent with the higher positive charge on the complex. From the obtained yield (0.33 g), it is clear that the product is not $[ReO(OH)(ImH)_4](I)_2$, but it could correspond to essentially quantitative conversion to $[ReO(OH)(ImH)_4](I_3)_2$ or a mixed I_3^-/I^- salt.

$[ReO(OH)(1\text{-}MeIm)_4](I)_2$ behaved similarly, giving a ν(Re═O) IR band at 955 cm^{-1} and ^1H NMR signals (DMSO-d_6) at 8.01 (H2), 7.50 (H5), 6.94 (H4), 3.86 (N−CH_3) ppm. $[ReO(OH)(1,2\text{-}Me_2Im)_4]^{2+}$ is

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(10) Ciani, G. F.; D'Alfonso, G.; Romiti, P. F.; Sironi, A.; Freni, M. *Inorg. Chim. Acta* **1983**, *72*, 29.

(11) Brewer, J. C.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 3334.

(12) Ciani, G.; Sironi, A.; Beringhelli, T.; D'Alfonso, G.; Freni, M. *Inorg. Chim. Acta* **1986**, *113*, 61.

(13) Freni, M.; Giusto, D.; Romiti, P.; Minghetti, G. *Gazz. Chim. Ital.* **1969**, *99*, 286.

Table 1. Crystallographic Data for Structures **I**−**IV**

	$[ReO_2(2\text{-}MeImH)_4][B(C_6H_5)_4]\cdot 3CH_3OH$ (**I**)	$[ReO_2(1\text{-}MeIm)_4][B(C_6H_5)_4]\cdot H_2O\cdot 0.5CH_3OH$ (**II**)	$[ReO_2(5\text{-}MeImH)_4]$-$[B(C_6H_5)_4]$ (**III**)	$[ReO(OH)(1,2\text{-}Me_2Im)_4]$-$(I_3)_{0.5}(ReO_4)_{1.5}$ (**IV**)
mol formula	$C_{43}H_{56}BN_8O_5Re$	$C_{40.5}H_{48}BN_8O_{3.5}Re$	$C_{40}H_{44}BN_8O_2Re$	$C_{20}H_{33}I_{1.5}N_8O_8Re_{2.5}$
fw	961.99	899.90	865.86	1169.42
a, Å	10.696(3)	15.619(2)	10.199(2)	23.290(8)
b, Å	15.128(4)	9.486(2)	13.441(5)	10.863(7)
c, Å	15.497(4)	27.387(4)	28.798(10)	25.709(8)
α, deg	113.57(2)	90	90	90
β, deg	97.25(2)	97.09(1)	90	94.36(3)
γ, deg	95.94(2)	90	90	90
V, Å^3	2247.1(1)	4026.7(12)	3948(2)	6486(5)
Z	2	4	4	8
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 4)	$P2_12_12_1$ (No. 19)	$I2/a$ (No. 15)
temp, °C	20	−58	−98	−58
λ, Å	0.709 30 (Mo Kα)	1.541 78 (Cu Kα)	1.541 78 (Cu Kα)	1.541 78 (Cu Kα)
ρ_{calcd}, g cm^{-3}	1.422	1.484	1.457	2.395
μ, cm^{-1}	27.9	60.6	61.3	290.4
transm coeff	0.50−0.72	0.14−0.34	0.46−0.68	0.08−0.36
R^a	0.030	0.057	0.043	0.060
$R_w{}^a$	0.029	0.062	0.046	0.060

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

very sensitive to ligand loss, and an iodide salt could not be isolated, although a stable salt was obtained when $Na[B(C_6H_5)_4]$ was added early to the mixture, before the imidazolium cation began to appear (see below).

$[ReO(OH)L_4]^{2+}$ Tetraphenylborates. $[ReO(OH)(1,2\text{-}Me_2Im)_4]$-$[B(C_6H_5)_4]_2$ was isolated when $[ReO_2(1,2\text{-}Me_2Im)_4]I$ (1.24 g, 1.71 mmol) was dissolved in methanol (20 mL) and protonated by addition of a methanol solution of HBF_4 (3.4 mL, 2.51 mmol). The protonated complex was immediately precipitated by adding $Na[B(C_6H_5)_4]$ (1.29 g, 3.77 mmol) as a concentrated methanol solution. The purple solid was filtered and washed with ethanol until the filtrate lost its yellow color; yield, 1.515 g (70%). IR (CsI; cm^{-1}): 962 (m, br) ν(Re═O). ^{13}C CP/MAS (ppm): δ 1,2-Me$_2$Im, 148.1 (C2), 128.8 (C4), 122.7 (C5), 33.8 (N−CH$_3$), 11.0 (C−CH$_3$); $B(C_6H_5)_4^-$, 164.2, 136.0, 125.7. Anal. Calcd for $C_{68}H_{78}B_2N_8O_2Re$: C, 65.75; H, 5.92; B, 1.74; N, 9.02. Found: C, 65.22; H, 5.81; B, 1.66: N, 9.03.

The same method applied to $[ReO_2(1\text{-}MeIm)_4]^+$ yielded a solid whose microanalysis corresponds to $[ReO(OH)(1\text{-}MeIm)_4][B(C_6H_5)_4]_{4/3}$-$(BF_4)_{2/3}$. IR (CsI; cm^{-1}): 973 (m) ν(Re═O). ^{13}C CP/MAS (ppm): δ 1-MeIm, 137.0 (C2), 126.7 (C4), 123.6 (C5), 33.1 (N−CH$_3$); $B(C_6H_5)_4^-$, 166.9, 141.2, ∼ 127 (interference from ligand). Anal. Calcd for $C_{48}H_{51.7}B_2N_8O_2ReF_{2.7}$: C, 55.92; H, 5.05; B, 2.10; N, 10.87. Found: C, 56.08; H, 5.14; B, 1.85; N, 10.89. It is unclear whether this sample is a mixture of the BF_4^- and $B(C_6H_5)_4^-$ salts or a single crystalline phase with partial BF_4^- substitution like the I_3^-/ReO_4^- salt described in this paper.

Protonation of $[ReO_2L_4]^+$ Solutions. Protonation of $[ReO_2(1\text{-}MeIm)_4]I$ was followed spectrophotometrically in methanol by recording spectra (200−350 nm) of $\sim 10^{-5}$ M solutions at room temperature as a function of pH. Under these conditions, equilibrium H^+ concentrations are essentially equal to added HBF_4.

Protonation of $\sim 10^{-3}$ M solutions of $[ReO_2(1\text{-}MeIm)_4]I$ and $[ReO_2(1,2\text{-}Me_2Im)_4]I$ in aqueous solutions was monitored from the weaker d−d spectral region (300−900 nm). Data were obtained in the +7 to −4 pH range for the 1-MeIm complex and in the +8 to −8 pH range for the 1,2-Me$_2$Im complex. For HCl concentrations < 0.1 M, pH was measured using a combined glass/calomel electrode calibrated just before use with standard buffers (pH 4 and 7). Acidities for higher concentrations of HCl and H_2SO_4 were expressed in terms of Hammett's acidity function $|H_o|$.[14] Each data point was collected on a fresh solution, and absorbance was measured 2−3 min after dissolution. Measurements at intermediate acidities for the determination of K_{a_1} of the 1-MeIm complex were obtained at 3 °C using an ice-water-cooled cell. Since temperature had no effect on the more acidic solutions, the data to estimate K_{a_2} were obtained at room temperature. The more stable $[ReO_2(1,2\text{-}Me_2Im)_4]I$ complex could be studied at room temperature over the entire pH range. In both cases, decomposition to an insoluble black material occurred at acidities above pH −4.

Crystallographic Measurements and Structure Determination. X-ray work for all compounds was carried out on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized copper radiation. The reduced triclinic cell was obtained from 15−25 reflections found on a rotation photograph. Conversion to the conventional cell, when needed, was then made in accordance with the Niggli matrix. The cell parameters given in Table 1 were calculated from 25 higher-angle reflections. Laue symmetry was eventually checked by comparing intensities between the various octants. Systematic absences were determined by inspection of the full data set.

In all cases, intensity data ($2\theta_{max} = 140°$) were collected over more than the minimum number of octants required by Laue symmetry. The orientation was monitored every 200 measurements, and the intensity was checked every 60 min with four to six standard reflections. Data were corrected for the effects of Lorentz, polarization, and absorption[15] (Gaussian integration, 10 × 10 × 10 grid).

Structure determination for $[ReO(OH)(1,2\text{-}Me_2Im)_4](I_3)_{0.5}(ReO_4)_{1.5}$ raised particular problems, which are discussed below. The three other structures were solved by the heavy-atom method. The Re atoms were located from a Patterson map. All other non-hydrogen atoms were located by successive ΔF maps. Refinement was anisotropic for all non-hydrogen atoms. Non-methyl hydrogen atoms were calculated at idealized positions (0.95 and 0.85 Å for C−H and N−H, respectively). The thermal parameters B(H) were fixed at [B(non-H) + 1] Å^2. One hydrogen of each methyl group was located from the ΔF map, the others were placed at idealized positions. Hydrogen parameters were not refined, but their positions were recalculated after each cycle. Details specific to each structure are given below. Refinement was done using NRCVAX[15] and SHELX-76.[16] In the latter case, the atomic scattering factors and anomalous dispersion terms (Re, I) were taken from standard sources.[17−19] Full sets of atom parameters are provided in the supporting information.

$[ReO_2(2\text{-}MeImH)_4][B(C_6H_5)_4]\cdot 3CH_3OH$ (I). A thick yellow plate (0.13 × 0.38 × 0.49 mm^3) was used for the X-ray diffraction study. The whole sphere (15774 intensity measurements) was averaged to 7887 unique hkl, $hk\bar{l}$, $\bar{h}kl$, and $\bar{h}k\bar{l}$ reflections (R_{int} = 0.026), of which 6127 with $I/\sigma(I) \geq 3$ were used for structure determination. The structure

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(14) Rochester, C. H. *Organic Chemistry: A Series of Monograms*; Academic Press: London, U.K., 1970; Vol. 17, p 38.

(15) Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L. *J. Appl. Crystallogr.* **1989**, *22*, 1021.

(16) Sheldrick, G. M. *SHELX-76, Crystallographic Program System*; University of Cambridge: Cambridge, England, 1976.

(17) Cromer, D. T.; Libermann, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(19) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

solved and refined well in the centric $P\bar{1}$ space group. No disorder was detected. The hydroxyl hydrogens of the lattice methanol molecules were located from the ΔF map, and their positions and temperature factors were refined. A few electron-density peaks in the range −0.63 to +0.42 e/Å^3 remained near the Re atom in the final ΔF map.

$[ReO_2(1\text{-}MeIm)_4][B(C_6H_5)_4]\cdot H_2O\cdot 0.5CH_3OH$ (II). The crystal used for the X-ray work was a brick-red prism (0.24 × 0.34 × 0.60 mm^3). A total of 15 267 reflections (hkl, $hk\bar{l}$, $\bar{h}kl$, $\bar{h}k\bar{l}$) were averaged to 7639 unique hkl and $hk\bar{l}$ reflections ($R_{int} = 0.055$), of which 6446 with $I/\sigma(I) \geq 3$ were used for structure determination. Space group $P2_1/n$ was uniquely determined from Laue symmetry and systematic absences. The non-hydrogen atoms in $[ReO_2(1\text{-}MeIm)_4]^+$ and $[B(C_6H_5)_4]^-$ were well-ordered, but disorder was found to be present in two different regions containing lattice solvent molecules.[20] Residual peaks within ±0.60 e/Å^3 remained in the final ΔF map near the metal center.

$[ReO_2(5\text{-}MeImH)_4][B(C_6H_5)_4]$ (III). A brick-red prism of dimensions 0.14 × 0.19 × 0.26 mm^3 was used for the data collection. A set of 14 440 $hk\bar{l}$, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$, and $\bar{h}\bar{k}\bar{l}$ reflections was measured. Out of the 7483 hkl and $\bar{h}\bar{k}\bar{l}$ obtained after averaging ($R_{int} = 0.056$), 6336 with $I/\sigma(I) \geq 3$ were used in the structural study. The space group was defined uniquely from Laue symmetry and systematic absences. No evidence of disorder, such as that resulting from imidazole binding as the 4-methyl, instead of the 5-methyl, tautomer, was detected. The absolute configuration was determined using the BIVOET routine of the NRCVAX program.[21] Residual peaks within ±1.3 e/Å^3 remained near the metal center.

$[ReO(OH)(1,2\text{-}Me_2Im)_4](I_3)_{0.5}(ReO_4)_{1.5}$ (IV). These crystals were obtained as a side product during attempts to prepare $ReO(OEt)I_2(1,2\text{-}Me_2Im)_2$ as described for pyridine analogues.[22] Concentrated HBF_4 (2.5 mL, 13.8 mmol) was added to a suspension of $[ReO_2(1,2\text{-}Me_2Im)_4]I\cdot 2CH_3OH$ (1.88 g, 2.60 mmol) in ethanol (100 mL), and the purple solution was refluxed for 90 min. The very dark blue solution was cooled to room temperature, and a black solid was filtered and washed with diethyl ether. By recrystallization from ethanol, a small amount of royal-blue diamond-shaped crystals suitable for X-ray diffraction were obtained. This complex is clearly a minor component of the black mixture.

A small crystal (0.058 × 0.058 × 0.076 mm^3) was used for X-ray work. An entire sphere (22 974 reflections) was collected, which was averaged to 6155 unique hkl and $hk\bar{l}$ reflections. The standards decayed by 16% during data collection, and scaling did not perfectly correct for decomposition, as indicated by the relatively high R_{int} value (0.147). The data with $I/\sigma(I) \geq 3$ totaled 2509 reflections. Space groups $I2/a$ and Ia were consistent with Laue symmetry and systematic absences (hkl, $h + k + l \neq 2n$; $h0l$, h, $l \neq 2n$; $0k0$, $k \neq 2n$). The structure was solved and refined in the centric $I2/a$ space group. The unexpected presence of ReO_4^- and disorder made the Patterson map difficult to unravel, but some of the Re and I atoms could be located. The remaining non-hydrogen atoms were found from ΔF maps. The anions providing the −2 charge should actually be represented as $(I_3)_{0.5}(ReO_4)_{0.5}(ReO_4)$. The triiodide anions are not disordered, but both types of ReO_4^- are.[20] Refinement was anisotropic for Re and I atoms and isotropic for C, N, and O atoms. Hydrogen atoms were treated as they were in the previous structures. Residual electron density within ±0.78 e/Å^3 was located near Re and I atoms.

Results

trans-Dioxo compounds $[ReO_2L_4]I$ of imidazoles were prepared by adapting the method developed by Brewer and Gray[11] for $[ReO_2py_4]I$. Yields generally >70% were obtained by reacting $ReO_2I(PPh_3)_2$ with 4−20 equiv of the ligand in methanol. The more basic imidazoles reacted much faster than pyridines. Almost instantaneous change in color indicated that the reaction had taken place quickly at room temperature. Nevertheless, the mixture was heated for a short time to ensure complete reaction. To obtain samples with better crystallinity, attempts were made to replace the counterion by adding NH_4PF_6 or NH_4BF_4 to $[ReO_2L_4]I$ in methanol. However, the samples were contaminated by the NH_4^+ salt when a large excess was added, or only partial replacement occurred when a stoichiometric amount or a small excess was used. A typical example is $[ReO_2(5\text{-}MeImH)_4](PF_6)_{0.94}(I)_{0.06}$, whose composition was deduced from an X-ray crystallographic study.[23] However, clean conversion to less soluble $B(C_6H_5)_4^-$ salts could be achieved.

Spectroscopic Data of *trans*-Dioxo Complexes. The O═Re═O unit gives rise to strong characteristic features in both infrared and Raman spectra. For all of our $[ReO_2L_4]X$ compounds with imidazoles and the chloride salts described earlier,[6] the ν_{as}(O═Re═O) band is found between 765 and 794 cm^{-1}. This is comparable with the frequencies reported for $[ReO_2(CN)_4]^{3-}$ [24] and *trans*-ReO_2N_4 cores with cyclam[25−28] and azaindole.[29] This vibration tends to appear at 810−825 cm^{-1} for complexes with pyridines and aliphatic amines.[30−33] The Raman active ν_s(O═Re═O) vibration was found in the 900−925 cm^{-1} range, in agreement with the value (905 cm^{-1})[8] calculated from the luminescence spectrum of $[ReO_2(1\text{-}MeIm)_4]^+$. For $[ReO_2py_4]^+$, a frequency of 916 cm^{-1} was observed in acetonitrile solution[34] and calculated from luminescence spectra.[1]

The electronic spectra of the *trans*-dioxo imidazole complexes exhibit three major components. The high-energy region below 225 nm includes imidazole $\pi \rightarrow \pi^*$ transitions.[35] The absorption near 260 nm (ϵ = 6000−10 000 M^{-1} cm^{-1}) probably has the same origin as the 331 nm band ($\epsilon \sim$ 25 000 M^{-1} cm^{-1}) of the corresponding pyridine complex, which has been attributed to a $[d_{xy} \rightarrow \pi_L^*]$ MLCT transition.[11] Finally, the third absorption found in the visible region (467 nm) is due to a ligand field $^1A_{1g}[(b_{2g})^2] \rightarrow {}^1E_g[(b_{2g})^1(e_g)^1]$ transition. It was found at 445 nm in the pyridine complex.

The NMR data given in the experimental section follow the trend discussed in a previous study.[6] The ^{13}C chemical shifts as assigned in the C2 > C4 > C5 order as noted by other

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(20) A full description of the disorder is available in the Supporting Information.

(21) Hynes, R. C.; Le Page, Y. *J. Appl. Crystallogr.* **1991**, *24*, 352.

(22) Ram, M. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 130.

(23) $[ReO_2(5\text{-}MeImH)_4](PF_6)_{0.94}(I)_{0.06}$ was obtained from metathesis of the corresponding iodide with 2 equiv of NH_4PF_6 in methanol. Dark red crystals formed after several days. The orthorhombic unit cell ($P2_12_12$, a = 12.225(5) Å, b = 20.617(6) Å, c = 11.031(6) Å, Z = 4) contains $[ReO_2L_4]^+$ in which all ligands exist as the 5-MeImH tautomer. The counterions occupy two sets of 2-fold special positions, in one of which PF_6^- is replaced 12% of the time by I^-. The two types of PF_6^- are disordered, most of the F atoms being distributed over two or three positions. The structure could not be refined below R = 0.07, and the more reliable crystallographic study on the BPh_4^- salt is reported here.

(24) Howard-Lock, H. E.; Lock, C. J. L.; Turner, G. *Spectrochim. Acta* **1982**, *38A*, 1283.

(25) Winckler Tsang, B.; Reibenspies, J.; Martell, A. E. *Inorg. Chem.* **1993**, *32*, 988.

(26) Luna, S. A.; Bolzati, C.; Duatti, A.; Zucchini, G. L.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1992**, *31*, 2595.

(27) Blake, A. J.; Greig, J. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2645.

(28) Wang, Y. P.; Che, C. M.; Wong, K. Y.; Peng, S. M. *Inorg. Chem.* **1993**, *32*, 5827.

(29) Lebuis, A. M.; Beauchamp, A. L. *Can. J. Chem.* **1993**, *71*, 2060.

(30) Jezowska-Trzebiatowska, B.; Hanuza, J.; Baluka, M. *Spectrochim. Acta* **1971**, *27A*, 1753.

(31) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054.

(32) Johnson, J. W.; Brody, J. F.; Ansell, G. B.; Zentz, S. *Inorg. Chem.* **1984**, *23*, 2415.

(33) Beard, J. H.; Casey, J.; Murmann, R. K. *Inorg. Chem.* **1965**, *4*, 797.

(34) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889.

(35) Grebow, P. E.; Hooker, T. H., Jr. *Biopolymers* **1975**, *14*, 871.

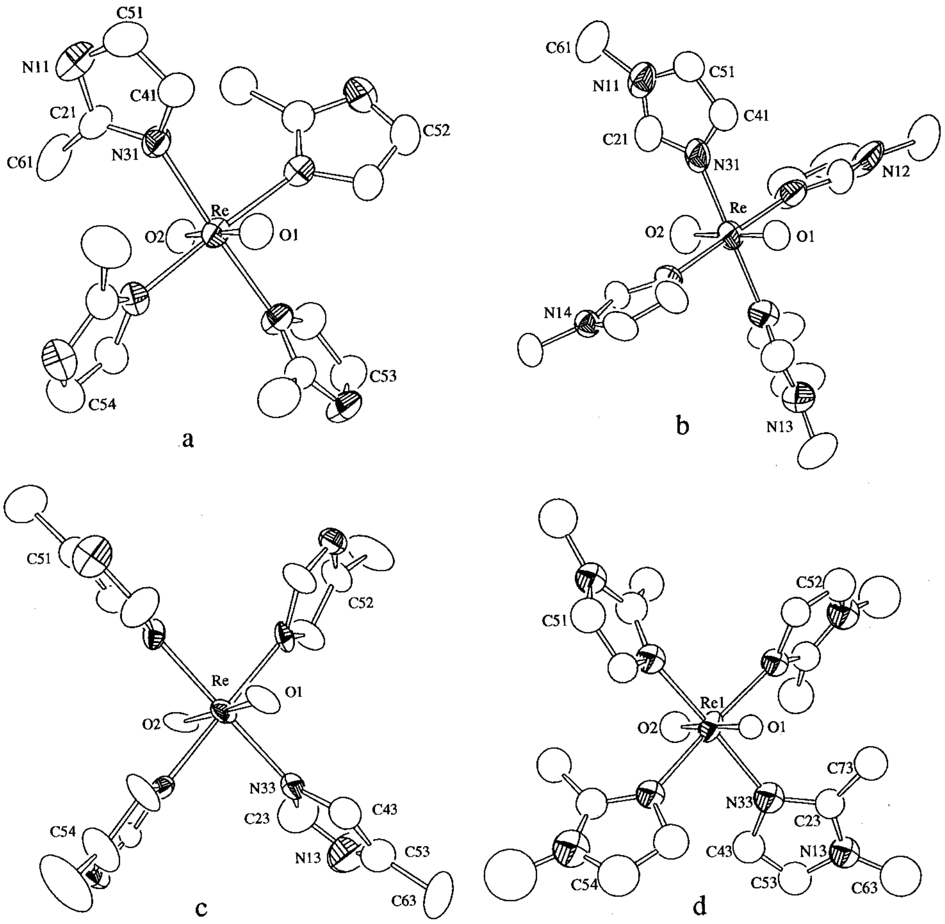

Figure 1. ORTEP drawings showing numbering schemes for (a) $[ReO_2(2\text{-MeImH})_4]^+$ (**I**), (b) $[ReO_2(1\text{-MeIm})_4]^+$ (**II**), (c) $[ReO_2(5\text{-MeImH})_4]^+$ (**III**), and (d) $[ReO(OH)(1,2\text{-Me}_2Im)_4]^{2+}$ (**IV**). Thermal ellipsoids drawn at the 50% probability level. H atoms omitted for simplicity.

workers.[36,37] C4/C5 averaging due to fast tautomeric exchange in non-*N*-methylated ligands is removed by complexation.

Most of our ^1H NMR spectra were run in D_2O. The lowest-field signal is found for H2, when present, at 7.6−7.8 ppm, whereas H4 and H5 occur in the 6.8−7.3 ppm range, H5 appearing ∼0.2 ppm downfield from H4. However, the spectra are solvent sensitive. For related $[TcO_2L_4]^+$ in CD_3OD,[7] H2 was found at lower field and the H4−H5 separation was much smaller, an unresolved H4/H5 signal being observed for the 1-MeIm complex. This is consistent with our observations for $[ReO_2(1\text{-MeIm})_4]^+$: the 7.65 (H2), 6.99 (H4), and 7.20 (H5) ppm signals for the iodide salt in D_2O are displaced to 7.73 (H2) and 7.10/7.11 (H4/H5) ppm, respectively, for the $B(C_6H_5)_4^-$ salt in methanol. For $[TcO_2(1\text{-MeIm})_4]^+$, H4 was assigned downfield from H5: the order of these resonances is not likely to be changed by solvent effect, and these assignments should be interchanged.

In all cases, various rotamers could exist since a 2-fold rotation of the ligand about the Re−N bond generates two non-equivalent configurations (see crystallographic work below). However, NMR provides no evidence for multiple rotamers in solution, either because one rotamer is favored or, more likely, because all ligands become equivalent by fast interconversion.

The situation is more complex with 4(5)-MeIm, which can coordinate as the 4-MeIm or 5-MeIm tautomers and produce various $[ReO_2(5\text{-MeIm})_n(4\text{-MeIm})_{4-n}]^+$ isomers. In fact, the ^1H NMR spectrum of a fresh CD_3OD of the $B(C_6H_5)_4^-$ salt shows, in addition to the highly predominant set of signals, a series of very weak peaks that could be due to such isomers. However, since the homogeneous crystalline material used for X-ray diffraction was shown to contain only $[ReO_2(5\text{-MeImH})_4]^+$ and this isomer was the only one detected in the solid state for $[Co(NH_3)_5(5\text{-MeImH})]Cl_3{\cdot}2H_2O$[36] and $[Cu(IDA)(5\text{-MeImH})]$ (IDA = iminodiacetate dianion),[38] the strong signals can confidently be assigned to the isomer containing only the remote 5-MeImH tautomer. The ^1H spectrum of the CD_3OD solution (7.59 (H2), ∼6.84 (H4), and 2.20 (CH_3) ppm) being similar to the one reported for the Tc analogue (7.76, 6.88 and 2.17 ppm), the latter species should also be formulated as the $[TcO_2(5\text{-MeImH})_4]^+$ isomer, rather than $[TcO_2(4\text{-MeImH})_4]^+$ as proposed.[7]

Crystal Structures of the *trans*-Dioxo Complexes. The structures of $[ReO_2(2\text{-MeImH})_4][B(C_6H_5)_4]{\cdot}3CH_3OH$ (**I**), $[ReO_2(1\text{-MeIm})_4][B(C_6H_5)_4]{\cdot}H_2O{\cdot}0.5CH_3OH$ (**II**), and $[ReO_2(5\text{-MeImH})_4][B(C_6H_5)_4]$ (**III**) were determined. ORTEP drawings of the three $[ReO_2L_4]^+$ ions are shown in Figure 1. Selected distances and angles are listed in Table 2. The Re═O distances in the 2-MeImH and 5-MeImH compounds lie in the 1.761−1.769 Å range typical of such complexes.[6,27−29,32,39−41] The

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(36) Henderson, W. W.; Shepherd, R. E.; Abola, J. *Inorg. Chem.* **1986**, *25*, 3157.

(37) Costes, J. P.; Commenges, G.; Laurent, J. P. *Inorg. Chim. Acta* **1987**, *134*, 237.

(38) Campos, A. C.; Busnot, A.; García, M. E. A.; Zafra, A. G. S.; Pérez, J. M. G.; Gutiérrez, J. N. *Inorg. Chim. Acta.* **1994**, *215*, 73.

(39) Lock, C. J. L.; Turner, G. *Acta Crystallogr.* **1978**, *B34*, 923.

(40) Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1971**, *10*, 2352.

(41) Glowiak, T.; Kubiak, M.; Jezowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1977**, *25*, 271. Lis, T.; Glowiak, T.; Jezowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1975**, *23*, 417. Glowiak, T.; Lis, T.; Jezowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1972**, *20*, 957. Sergienko, V. S.; Porai-Koshits, M. A.; Khodashova, T. S. *Zh. Strukt. Khim.* **1974**, *15*, 275.

Table 2. Comparison of Selected Bond Lengths (Å) and Angles (deg) for the Complex Cations

	$[ReO_2(2\text{-MeImH})_4]^+$ (**I**)	$[ReO_2(1\text{-MeIm})_4]^+$ (**II**)	$[ReO_2(5\text{-MeImH})_4]^+$ (**III**)	$[ReO(OH)(1,2\text{-Me}_2Im)_4]^{2+}$ (**IV**)
Re−O1	1.768(3)	1.749(5)	1.769(7)	1.896(13)[a]
Re−O2	1.761(3)	1.782(6)	1.763(7)	1.732(15)
Re−N31	2.138(3)	2.112(7)	2.111(8)	2.137(20)
Re−N32	2.137(4)	2.120(6)	2.132(8)	2.106(21)
Re−N33	2.146(3)	2.138(7)	2.140(9)	2.117(22)
Re−N34	2.148(3)	2.113(5)	2.108(8)	2.139(22)
O1−Re−O2	178.13(13)	179.5(2)	175.5(4)	179.1(7)
O1−Re−N31	89.88(13)	89.6(2)	87.9(3)	84.3(7)
O1−Re−N32	87.76(14)	89.9(3)	90.9(3)	86.7(7)
O1−Re−N33	90.57(14)	89.2(3)	92.5(4)	86.1(7)
O1−Re−N34	89.56(14)	89.4(2)	88.1(3)	85.1(7)
O2−Re−N31	91.99(13)	90.1(2)	89.0(3)	95.7(8)
O2−Re−N32	92.09(14)	89.8(3)	92.3(3)	94.2(8)
O2−Re−N33	87.56(14)	91.1(3)	90.7(3)	93.8(8)
O2−Re−N34	90.54(14)	91.0(2)	88.8(3)	94.0(8)
N31−Re−N32	92.01(13)	90.4(3)	88.1(3)	94.4(8)
N31−Re−N33	178.20(14)	178.8(3)	179.2(3)	168.9(8)
N31−Re−N34	89.34(13)	90.4(2)	92.2(3)	86.0(8)
N32−Re−N33	86.26(13)	89.8(3)	91.1(3)	90.7(8)
N32−Re−N34	176.99(13)	178.9(2)	88.5(3)	171.7(8)
N33−Re−N34	92.41(13)	89.4(2)	178.8(3)	87.6(8)
Re−N31−C21	130.1(3)	126.2(5)	127.8(7)	127.8(18)
Re−N31−C41	123.2(3)	127.0(5)	129.5(7)	120.5(16)
Re−N32−C22	130.6(3)	127.2(6)	123.5(7)	133.6(17)
Re−N32−C42	123.2(3)	127.0(6)	129.0(7)	123.1(15)
Re−N33−C23	130.0(3)	126.1(6)	128.5(8)	131.6(18)
Re−N33−C43	122.9(3)	130.2(7)	126.8(8)	122.4(17)
Re−N34−C24	129.3(3)	126.4(4)	130.0(7)	130.5(18)
Re−N34−C44	123.7(3)	127.6(5)	124.1(6)	122.2(17)

[a] The Re1 atom is involved.

Table 3. O1−Re−N3−C(α) Torsion Angles (deg) Describing Ring Orientation in Crystal Structures[a]

	ring 1	ring 2	ring 3	ring 4	ref
$[ReO_2(1\text{-MeIm})_4]^+$	20 [C4]	−4 [C2]	1 [C4]	38 [C2]	this work
$[ReO_2(5\text{-MeImH})_4]^+$	−16 [C2]	−41 [C2]	6 [C4]	20 [C4]	this work
$[TcO_2(1\text{-MeIm})_4]^+$	−22 [C2]	19 [C2]	22 [C4]	−19 [C4]	7
$[TcO_2(ImH)_4]^+$	14 [C4]	6 [C2]	−14 [C2]	−6 [C4]	7
$[ReO_2(2\text{-MeImH})_4]^+$	29 [C4]	46 [C4]	35 [C2]	34 [C2]	this work
$[ReO(OH)(1,2\text{-Me}_2Im)_4]^{2+}$	−44 [C4]	−42 [C4]	−50 [C2]	−35 [C4]	this work
$[ReO(O/OH)(1,2\text{-Me}_2Im)_4]^{+/2+}$	−36 [C2]	−36 [C4]	−36 [C2]	−36 [C4]	6
	−46 [C4]	−46 [C2]	−46 [C4]	−46 [C2]	
$[ReO_2py_4]^+$	−26	20	−18	18	39
$[ReO_2(4\text{-Mepy})_4]^+$	−6	−21	6	21	32
	17	−6	−17	6	
$[TcO_2(4\text{-}(t\text{-Bu})py)_4]^+$	15	12	−15	−12	43
	17	−6	−17	6	

[a] The four torsion angles are calculated with respect to the same oxo atom, and the α-carbon is chosen so as to keep the angle in the $-90° \le \tau \le 90°$ range. For imidazoles, the α-carbon involved is identified in brackets.

slight differences (1.749(5) and 1.782(6) Å) observed for the 1-MeIm complex could be an artifact due to disorder in the solvent molecules hydrogen-bonded to the oxo groups. The 12 independent Re−N distances, ranging from 2.111 to 2.148 Å, are also similar to those found in complexes with other N-heterocycles. The angles correspond within 3° to a regular octahedron, the only exception being the O═Re═O angles of 175.5(4)° in the 5-MeImH complex.

In the 1-MeIm and 5-MeImH compounds, coordination takes place along the lone pair direction, as evidenced from the approximately equal Re−N3−C2 and Re−N3−C4 angles (Table 2). On the other hand, for the C2-methylated complex, the Re−N3−C2 angles (129.3−130.6°) are, on average, 7° greater than the Re−N3−C4 angles (122.9−123.7°). Steric strain is also revealed by the N−C2−CH_3 angles: N3−C2−C6 is 3.2−7.0° greater than N1−C2−C6 (Supporting Information). Both of these distortions, which have been noted for other systems,[42] tend to displace the methyl group away from the O═Re═O axis. Steric hindrance also affects the overall complex conformation by rotating the imidazole ligands about the Re−N bond. As shown by the torsion angles listed in Table 3, in the absence of a 2-methyl group, at least three and often all four imidazole rings are roughly aligned with the O═Re═O direction ($-22° \le \tau \le +22°$). The same trend is exhibited by compounds with pyridines, which are not α-substituted.[32,39,43] On the other hand, with 2-MeImH and 1,2-Me_2Im, the α-methyl group rotates the rings ~45° away from the O═Re═O direction and generates a propeller-like conformation. For imidazole ligands, there are two unequivalent ring orientations about the Re−N bond, corresponding to C2 being on the same side (*up*) as or opposite (*down*) to the reference Re═O bond, respectively. The structures listed in Table 3 do not follow a unique pattern:

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(42) Geiser, U.; Ramakrishna, B. L.; Willett, R. D.; Hulsbergen, F. B. Reedijk, J. *Inorg. Chem.* **1987**, *26*, 3750. Horrocks, W. D., Jr.; Ishley, J. N.; Whittle, R. R. *Inorg. Chem.* **1982**, *21*, 3270. Bencini, A.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1985**, *24*, 700. Phillips, F. L.; Shreeve, F. M.; Skapski, A. C. *Acta Crystallogr.* **1976**, *B32*, 687. Reedijk, J.; Verschoor, G. C. *Acta Crystallogr.* **1973**, *B29*, 721.

(43) Kastner, M. E.; Fackler, P. H.; Clarke, M. J.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4683.

the *up-up-down-down* and *up-down-up-down* sequences around the O═Re═O axis are the most common, but the *up-up-up-down* arrangement has been found in an oxo−hydroxo compound.

Views of molecular packing are given and commented on in the Supporting Information. Both oxo groups form hydrogen bonds in the three structures. In $[ReO_2(2\text{-}MeImH)_4][B(C_6H_5)_4]\cdot 3CH_3OH$, lattice MeOH molecules form strong hydrogen bonds with O···O separations of 2.64 and 2.69 Å. An extensive network of hydrogen bonds involving these MeOH molecules and imidazole N−H groups provides an important contribution to lattice cohesion. Hydrogen bonding is less extensive in $[ReO_2(1\text{-}MeIm)_4][B(C_6H_5)_4]\cdot H_2O\cdot 0.5CH_3OH$, since the imidazole is N-methylated, but the oxo groups retain weaker interactions with disordered water or MeOH molecules (2.79 Å). In solvent-free $[ReO_2(5\text{-}MeImH)_4][B(C_6H_5)_4]$, imidazole N−H groups act as donors in strong hydrogen bonds (N···O, 2.71 and 2.76 Å).

Unit cell packing has been compared for the above structures and the $[TcO_2(1\text{-}MeIm)_4]^+$ and $[TcO_2(ImH)_4]^+$ complexes.[7] $[ReO_2(2\text{-}MeImH)_4][B(C_6H_5)_4]\cdot 3CH_3OH$ differs from the other crystals by having the O═Re═O axes of all cations oriented approximately along the same direction. More commonly, in $[ReO_2(5\text{-}MeImH)_4][B(C_6H_5)_4]$ for instance, adjacent ions adopt mutually perpendicular orientations. In the case of $[ReO_2(1\text{-}MeIm)_4][B(C_6H_5)_4]\cdot H_2O\cdot 0.5CH_3OH$, an intermediate situation is observed: the cations are linked into a chain with which the O═Re═O units are roughly aligned, but adjacent chains are running in mutually perpendicular directions in the crystal.

Protonation of $[ReO_2L_4]^+$. $ReO(OEt)I_2py_2$ has been reported to form when $[ReO_2py_4]^+$ is refluxed in the presence of HI in ethanol.[22] With imidazoles, oxo−alkoxo compounds were not obtained under these conditions from either ethanol or methanol. As soon as HI is added, the solution takes the bright purple color of $[ReO(OH)L_4]^{2+}$ and salts can be isolated. A broad range of conditions was tested with methanol. If the solution is allowed to stand or if acid concentration is high, the color changes from purple to brownish red. Under refluxing conditions, decomposition is complete after 2−4 h. The decomposition products include free protonated ligand (identified from ^1H NMR), I_3^- and ReO_4^-, and an insoluble black material which has not been identified. Decomposition could not be totally avoided even under the mildest conditions used, making it difficult to isolate pure stoichiometric phases, probably because I^-, I_3^-, and ReO_4^- can be interchanged as counterions and lead to nonstoichiometric materials (see below) or salt mixtures. Decomposition similarly occurred when HBF_4 was used instead of HI. The $B(C_6H_5)_4^-$ salts are more stable but less soluble.

Even though the reactions were run in methanol, $[ReO(OMe)L_4]^{2+}$ is not formed in these samples isolated quickly after addition of acid. An oxo−methoxo species would be detected by NMR, since rhenium−oxygen bonds are not labile.[44] Re−OCH_3 exchange with CD_3OD to give Re−OCD_3 should not take place over the few minutes needed to record the spectrum and a high-field ^1H NMR signal should be found for the Re−OCH_3 group in fresh solutions. Similarly, any solvolysis of $[ReO(OH)L_4]^{2+}$ to $[ReO(OCD_3)L_4]^{2+}$ should produce an extra set of imidazole signals, which are not observed.[45]

In the infrared, the $[O{=}Re{-}OH]^{2+}$ core shows a well-defined ν(Re═O) band in the 957−973 cm^{-1} range, in agreement with the published results for $[ReO(OH)L_4]^{2+}$ species with ethylenediamine (981 cm^{-1}),[30,31] pyridines (945−975 cm^{-1})[33] and macrocyclic ligands (952−969 cm^{-1}).[25] The ν(O−H) band (3200−3500 cm^{-1}) is usually masked by bands due to lattice solvent. As to the ν(Re−OH) and δ(Re−O-H) modes, expected in the 550−575 and 800−1200 cm^{-1} ranges,[30] respectively, they are usually weak and not detected in the present case.

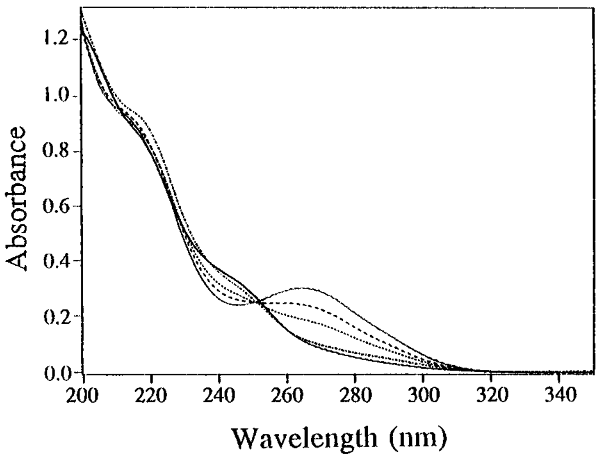

Figure 2. Protonation of $[ReO_2(1\text{-}MeIm)_4]I$ (3.30×10^{-5} M) with HBF_4 in methanol. H^+/Re ratio (from top to bottom at 270 nm): 0, 0.12, 0.23, 0.70, 1.10.

Upon protonation, the color of the complex changes from orange ($[O{=}Re{=}O]^+$) to purple ($[O{=}Re\text{-}OH]^{2+}$) to deep blue ($[O{=}Re{-}OH_2]^{3+}$). Protonation of $[ReO_2(1\text{-}MeIm)_4]I$ was studied in methanol at room temperature in the 200−350 nm spectral region. Figure 2 shows the changes in the UV region during the first protonation in methanol. As HBF_4 is added to the solution of the *trans*-dioxo complex, a net drop in the absorption near 265 nm occurs, while a slight increase near 240 nm is observed. Protonation is quantitative in methanol, since addition of excess HBF_4 results in loss of the isosbestic point at 250 nm (see $H^+/Re = 1.10$, Figure 2). In water, protonation is not quantitative in a 1:1 complex:HBF_4 mixture, but protonation can be achieved in concentrated acids (see below).

The effect of protonation on the UV−visible spectra parallels that observed for the pyridine analogue. In an aqueous solution, $[ReO_2(1\text{-}MeIm)_4]^+$ and $[ReO_2(1,2\text{-}Me_2Im)_4]^+$ show ligand-field bands at 431 nm ($\epsilon = 183\ M^{-1}\ cm^{-1}$) and 480 nm ($\epsilon = 321\ M^{-1}\ cm^{-1}$), respectively, characteristic of the $[O{=}Re{=}O]^+$ chromophore. This absorption moves to lower energies upon protonation ($[O{=}Re{-}OH]^{2+}$: 1-MeIm, 536 nm, $\epsilon = 148\ M^{-1}\ cm^{-1}$; 1,2-$Me_2Im$, 556 nm, $\epsilon = 287\ M^{-1}\ cm^{-1}$; $[O\text{-}Re\text{-}OH_2]^{3+}$: 1-MeIm, 624 nm; 1,2-$Me_2Im$, 683 nm). The corresponding values for the pyridine complex are as follows: $[O{=}Re{=}O]^+$, 445 nm, $\epsilon = 1200\ M^{-1}\ cm^{-1}$; $[O{=}Re{-}OH]^{2+}$, 504 nm, $\epsilon = 540\ M^{-1}\ cm^{-1}$; $[O{=}Re{-}OH_2]^{3+}$, 605 nm.[3]

The ligand-based transitions near 195 and 220 nm are not greatly influenced by the first protonation of an oxo ligand. The LMCT band of $[ReO_2(py)_4]^+$ moves from 331 nm to 297 nm upon protonation.[3] The 1-MeIm and 1,2-Me_2Im complexes exhibit the same behavior, the LMCT band moving to higher energies, from 255 to below 240 nm, where it gives rise to an intensity gain at ~220 nm.

The second protonation is more problematic, since 100% diprotonation is not reached at the highest acidity accessible (pH −4). The absorption near 500 nm (monoprotonated form)

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[44] Kashani, F. F.; Murmann, R. K. *Int. J. Chem. Kinet.* **1985**, *17*, 1007.

[45] The relevant point concerning oxo−methoxo species was raised by one of the reviewers. Although there is no evidence that $[ReO(OMe)L_4]^{2+}$ appears during the short residence times in solution used here, their formation over periods of days cannot be ruled out. This aspect could not be examined because an unidentified insoluble black solid precipitated. $[ReO(OH_2)L_4]^{3+}/[ReO(HOMe)L_4]^{3+}$ exchange in the trication could not take place under the conditions used here, all experiments being run in concentrated acids containing no methanol.

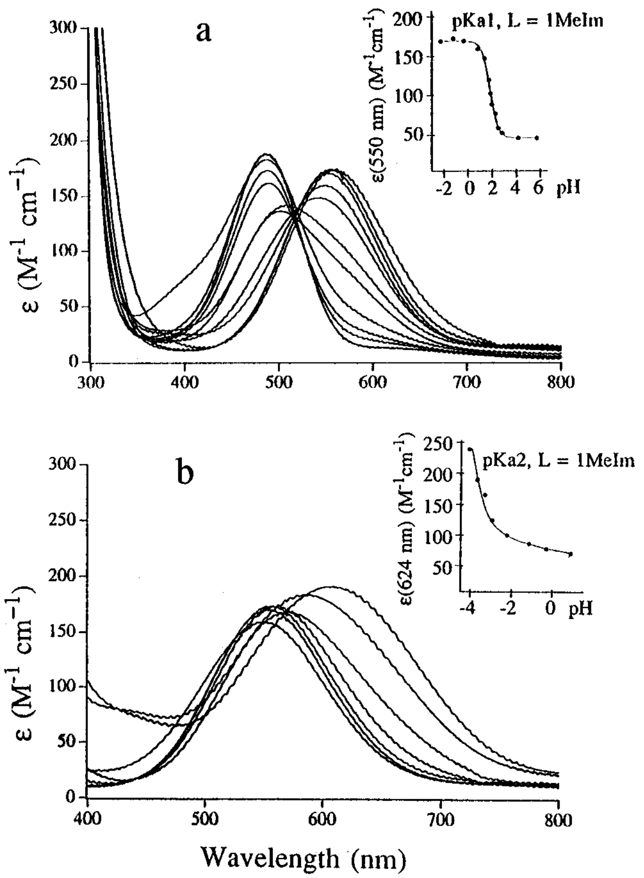

Figure 3. (a) Spectral changes accompanying the protonation of $[ReO_2(1\text{-}MeIm)_4]^+$. The pH varies from −1 to +6 from top to bottom at 550 nm. Inset: Absorbance measured at 550 nm. (b) Spectral changes accompanying the protonation of $[ReO(OH)(1\text{-}MeIm)_4]^{2+}$. The pH varies from −4 to +1 top to bottom at 624 nm. Inset: Absorbance at 624 nm.

never totally disappears as the absorption near 640 nm grows. At the same time, an intense band appears at ~325 nm and it trails in the visible, accounting for the greenish color of the solution (oxo−aqua complexes are expected to be blue).[46]

$[ReO(OH)L_4]^{2+}$ dissociates in water and NMR spectra were essentially those of $[ReO_2L_4]^+$. Spectra were recorded in DMSO, where the violet color indicates that the complex is still largely present in the $[ReO(OH)L_4]^{2+}$ form. The ^1H signals are shifted to a greater extent relative to the free ligand in DMSO than for the *trans*-dioxo species. Comparisons can be made between the $[ReO(OH)L_4]^{2+}$ and cobalt(III)−imidazole complexes.[36] For the latter complexes, the three ring protons were displaced downfield by complexation, the shifts being greater for H2 and H5 (*ca.* 0.5 ppm) than for H4 (*ca.* 0.15 ppm). Similar trends are followed by our protonated Re compounds: downfield shifts of 0.3/0.4 ppm were observed for H2 and 0.4/0.5 ppm for H5. The shift for H4 is large downfield (0.65 ppm) for 1,2-Me$_2$Im, smaller (0.08 ppm) for 1-MeIm and in the opposite direction (-0.08 ppm) for ImH. It should be noted, however, that, in the last case, these displacements are expressed with respect to the averaged H4/H5 signal of the ligand in fast tautomeric exchange.

Determination of Protonation Constants in Aqueous Solutions. The complexes are unstable in acidic solutions, decomposition producing visible spectral changes in both HCl and HBF_4 over periods of ~10 min. Results for $[ReO_2(1\text{-}MeIm)_4]^+$ and $[ReO_2(1,2\text{-}Me_2Im)_4]^+$, the least unstable complexes in the series, are described here.

Since spectra of very dilute solutions $\sim 10^{-5}$ M were particularly sensitive to decomposition, $\sim 10^{-3}$ M samples were used and protonation was studied in the visible ligand-field range (300−900 nm), where extinction coefficients are appropriate. Spectra were obtained for aqueous HCl solutions of pH from −4 to +7.

The acidity constant K_{a_1} (eq 1) of the monoprotonated species with 1-MeIm was determined at 3 °C, because decomposition took place much more slowly than at room temperature in the pH 2−6 range. The less sensitive 1,2-Me$_2$Im complex was

$$[O{=}Re{-}OH]^{2+} \rightleftharpoons [O{=}Re{=}O]^+ + H^+$$

$$K_{a_1} = ([O{=}Re{=}O]^+)(H^+)/([O{=}Re{-}OH]^{2+}) \qquad (1)$$

studied at room temperature. The changes in the visible region when the pH is varied from 6 to 1 are shown in Figure 3a. The pK_{a_1} values of 2.0 and ~3.8 were determined from the pH at half-neutralization in a plot of ε(550 nm) vs pH for the 1-MeIm and 1,2-Me$_2$Im complexes, respectively.

trans-Dioxo systems with chelating amines have pK_a's of ~3 (ethylenediamine, 3.3;[47,48] 1,3-diaminopropane, 3.2;[48] 1,4,8,11-tetraazacyclodecane, 2.95 [25]), whereas $[ReO_2(CN)_4]^{3-}$ protonates at pH 3.7−4.2[49] and $[ReO_2(CH_3NH_2)_4]^+$ is strongly acidic (pK_{a_1} = −0.43).[33] For a series of substituted pyridines, the protonation constant of the rhenium complex roughly follows that of the free ligand. The values for pyridine complexes typically range from −0.6 to +0.8 [2,33] with the 4-(dimethylamino)pyridine complex having a pK_{a_1} value of 2.3.[2]

$$[O{=}Re{-}OH_2]^{3+} \rightleftharpoons [O{=}Re{-}OH]^{2+} + H^+$$

$$K_{a_2} = ([O{=}Re{-}OH]^{2+})(H^+)/([O{=}Re{-}OH_2]^{3+}) \qquad (2)$$

The pK_{a_2} values were only estimated. At acidities above pH −4, dissolution in viscous H_2SO_4 is slow and decomposition to a black insoluble product occurs in the meantime. The spectral changes in the +1 to −4 pH range are shown in Figure 3b, as well as the ε(624 nm) vs pH curve for the 1-MeIm complex. Curve fitting over this limited pH range could not be applied in the absence of a clear plateau a high acidities to provide ε for $[O{=}Re{-}OH_2]^{3+}$. However, an approximate ε value of 450 M^{-1} cm^{-1} was obtained by quickly scanning the visible region of a solution in concentrated HBF_4, whose blue color indicated a very high degree of protonation. From the ε(624 nm) vs pH curve, pK_{a_2} can be estimated to be close to −4. Using the same strategy, a pK_{a_2} value of ~−4.1 was obtained for the second protonation of the 1,2-Me$_2$Im complex.

Literature records on the second protonation for related systems are scarce. To our knowledge, the only published data on rhenium systems are those for $[ReO_2(CN)_4]^{3-}$ (pK_{a_2} = 1.3−1.4)[49] and $[ReO_2(L{-}L)_2]^{3+}$ (L−L = ethylenediamine, −0.9;[47,48] 1,3-diaminopropane, −0.7 [48]). The imidazole complexes studied in this paper are definitely more acidic than these systems.

Crystal Structure of $[ReO(OH)(1,2\text{-}Me_2Im)_4](I_3)_{0.5}(ReO_4)_{1.5}$. The environment of the rhenium atom defines a distorted octahedron (Figure 1d). The two rhenium−oxygen bonds are not equivalent: Re=O2 (1.732(15) Å) is definitely shorter than Re−O1 (1.896(13) Å), and both significantly deviate from those found in the O=Re=O units. The difference between our Re−O1 and Re−O2 bond lengths is significant, although smaller than what has been observed (1.685(8) and 1.970(8)

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(46) Parker, D.; Roy, P. S.; *Inorg. Chem.* **1988**, *27*, 4127.

(47) Murmann, R. K.; Foerster, D. R. *J. Phys. Chem.*, **1963**, *67*, 1383.

(48) Lawrance, G. A.; Sangster, D. F. *Polyhedron* **1986**, *5*, 1553.

(49) Roodt, A.; Leipoldt, J. G.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1992**, *31*, 2864, and references cited therein.

Å) for $[ReO(OH)(O_1cyclam)]^+$ (where O_1cyclam = 1,4,8,11-tetraazacyclotetradecan-2-one).[25] However, it is in good agreement with those found for $[ReO(OH)(CN)_4]^{2-}$ (Re—O = 1.70(1) and 1.90(1) Å).[50] Clearly, the complex studied is the oxo−hydroxo complex and not the oxo−aqua ion: in the case of Re(V) oxo−aqua species, the long Re—O bond is much longer (2.142(7) Å).[51] The imidazole rings are tilted to minimize steric hindrance, and coordination does not take place along the lone pair direction, the Re—N3—C2 angles (mean 130.9°) being larger than Re—N3—C4 (mean 122.1°). I_3^- is linear by symmetry, and the I—I distance (2.925(3) Å) is normal.[52]

Discussion

trans-$[ReO_2L_4]I$ complexes were obtained in very high yields, and conversion to the tetraphenylborate salts provided clean samples suitable for X-ray diffraction. The iodides are also less prone to decomposition than the chlorides prepared earlier.

Generally speaking, the imidazole compounds form more readily than the pyridine analogues. The reaction with $ReO_2I(PPh_3)_2$ takes place within minutes, even under stoichiometric conditions, whereas longer reaction time and large excess have to be used with pyridines. The imidazole complexes are also less sensitive to decomposition, which can be ascribed to greater Re—N bond strength due to imidazoles being better σ-donors (pK_a of LH^+ ∼ 7) than pyridines (pK_a = 5−6).[53] Greater σ-donation also makes the Re center electron richer and reduces its ability to act as π-acceptor for the oxo group. As a consequence, the Re═O double bond character is decreased, as indicated by the ν_{as}(O═Re═O) IR stretching frequency (810 cm^{-1} for pyridine, 780 cm^{-1} for imidazole), whereas the oxo groups become more nucleophilic (greater pK_a of the $O{=}Re{-}OH^{2+}$ unit). In addition, imidazoles are less sterically demanding than pyridines: the ring being five-membered, the adjacent N—C bonds are displaced away from the Re—N bond and the substituents on the α-carbons more remote from the O═Re═O axis. These factors probably explain that stable complexes were obtained with 2-methylated imidazoles, whereas compounds with 2-substituted pyridines have not been reported.

The conformation of the complex is sensitive to the presence of a 2-methyl group: the ligands are rotated ∼45° with respect to the O═Re═O axis, although there is a clear trend among complexes with pyridines and other imidazoles to keep the rings roughly aligned (within 22°) with this direction. There are no particular constants in molecular packing that could explain this feature, since the available series of structures includes complexes with pyridines and imidazoles, various counteranions, and different lattice solvents present. This could reflect a certain degree of π-bonding in the Re—N bond. Johnson and coworkers[54] have proposed that imidazole can act as a π-donor in the iron(III)−cyano core, where metal d orbitals of suitable symmetry are available and a number of CN^- ligands can act as a good π-acceptor sink. The possibility of π-donation is less likely here, because the upright ligand orientation would require a participation of the filled d_{xy} orbital. Metal-to-ligand back-bonding remains possible, however, involving donation of the two electrons of the metal d_{xy} orbital into an empty imidazole π^*-level. Nevertheless, the effect would likely be small, since some non-2-substituted ligands deviate from the upright orientation in the crystal structures, the loss of this interaction in the 2-methylimidazole derivatives does not appreciably affect stability, and spectroscopic properties are similar for all systems.

Even though *trans*-dioxo imidazole complexes show greater stability towards ligand loss than those of pyridines, protonated ligand was detected in aged solutions of $[ReO_2(1,2\text{-}Me_2Im)_4]Cl$,[6] and some of our compounds sometimes showed small amounts of byproducts yet to be identified. Ligand dissociation was also noted for water solutions of $[TcO_2L_4]Cl$ (L = ImH, 1-MeIm, 4(5)-MeImH) even at pH 7.[7] Under the same conditions, free ligand was not usually detected in our samples, but, at intermediate pH (2−4), the complexes are not stable over long periods of time. Work is underway to determine the nature of these new species, which are probably those responsible for the spurious NMR signals.

Acknowledgment. We wish to thank M. Simard, F. Bélanger-Gariépy, and A. M. Lebuis for help in collecting the X-ray data and G. Timmins (McMaster University) for running the Raman spectra. Special thanks to M. Simard for help in solving the structure of the oxo−hydroxo complex and to C. Reber and C. Savoie for assistance with the UV−vis experiments. The financial support of the Natural Sciences and Engineering Research Council of Canada is also acknowledged.

Supporting Information Available: Figures showing views of molecular packing, tables listing final coordinates, temperature factors, bond lengths and angles, distances to the weighted least-squares planes for the four structures, and text describing solvent disorder for **II** (43 pages). Ordering information is given on any masthead page.

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(50) Purcell, W.; Roodt, A.; Basson, S. S.; Leipoldt, J. G. *Transition Met. Chem.* **1989**, *14*, 5.

(51) Purcell, W.; Roodt, A.; Basson, S. S.; Leipoldt, J. G. *Transition Met. Chem.* **1990**, *15*, 239.

(52) Bélanger, S.; Beauchamp, A. L. *Acta Crystallogr.* **1993**, *C49*, 388.

(53) Scriven, E. F. V. In *Comprehensive Heterocyclic Chemistry*; Katritzki, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, U.K., 1984; Vol. 2, Chapter 2.05. Grimmett, M. R. V. In *Comprehensive Heterocyclic Chemistry*; Katritzki, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, U.K., 1984; Vol. 5, Chapter 4.07.

(54) Johnson, C. R.; Jones, C. M.; Asher S. A.; Abola, J. E. *Inorg. Chem.* **1991**, *30*, 2120.