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Seven-Coordinate $[Re^{V}ON_4X_2]^+$ Complexes (X = O and Cl)[†]

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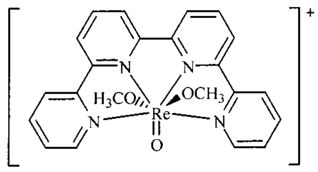
The oxorhenium(V) complexes with ligands containing N_4 (H_2pmen) and N_4O_2 (H_2bbpen, H_2Clbbpen, and H_2bped) donor atom sets have been synthesized. X-ray crystallographic analyses of the $[ReO(H_2pmen)Cl_2]^+$, $[ReO(bbpen)]^+$, and $[ReO(bped)]^+$ complexes showed that all three cations share a rare seven-coordinate structure with a distorted pentagonal bipyramidal geometry, which represents a novel and potentially general structural motif in $Re^{V}{=}O$ complexes. ^{1}H NMR spectroscopy shows that the structures of the complexes are retained in the solution.

Introduction

The coordination chemistry of rhenium attracts burgeoning interest partly because of its similarities to technetium, whose radionuclide (^{99m}Tc) is the workhorse of diagnostic nuclear medicine.[1−7] Recently, the radioisotopes ^{186}Re and ^{188}Re, which have suitable β-emitting properties, have been investigated for potential use in therapeutic nuclear medicine.[4,6] For example, a ^{186}Re complex with hydroxyethylidene diphosphonate (HEDP) has been proven to be beneficial in clinical trials for the palliation of bone pain.[4,6,8]

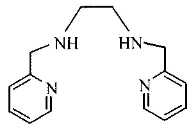
$Re^{V}{=}O$ complexes are almost exclusively five-coordinate (square pyramidal geometry) or six-coordinate (octahedral geometry). To our knowledge, there is only one seven-coordinate Re=O complex, $[ReO(qtp)(OCH_3)_2]ClO_4$, which has a distorted pentagonal bipyramidal geometry in which the N4 donor ligand qtp forms a five-membered basal plane with the oxo O and has two methoxides occupying axial positions.[9] This geometry is not seen in numerous other Re complexes containing pyridyl or polypyridyl ligands.[10−12]

Previously, our group has prepared various Re(V) and Tc(V) complexes with ligands containing neutral oxygen, anionic oxygen, and phosphorus donor atoms.[13−16] As a follow-up to those studies, seven-coordinate ReO complexes, sharing structural features similar to those in $[ReO(qtp)(OCH_3)_2]ClO_4$, have been prepared with aminopyridyl (H_2pmen), aminopyridylcarboxyl (H_2bped), and aminopyridylphenolate (H_2bbpen and H_2Clbbpen) ligands. They represent a unique structural motif in Re=O chemistry upon which we elaborate herein in a new series of seven-coordinate Re=O monocationic species which is, unexpectedly, quite general with the appropriate choice of multidentate ligands.

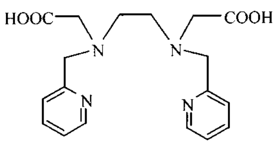


$[ReO(qtp)(OCH_3)_2]^+$

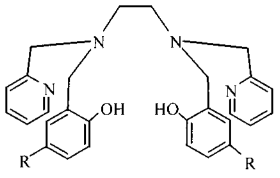
qtp = 2,2′:6′,2″:6″,2‴-quaterpyridine



H_2pmen



H_2bped



R = H, H_2bbpen
= Cl, H_2Clbbpen

Experimental Section

Materials. Ethylenediamine, salicylaldehyde, sodium borohydride, 2-picolyl chloride hydrochloride, hexadecyltrimethylammonium bromide, sodium hexafluorophosphate, and sodium hydroxide were

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[†] **Editor's Note:** An article on the same topic but with substantial errors in crystallographic content was posted ASAP on April 1, 2000, and temporarily withdrawn. This article replaces the withdrawn article with the crystallographic errors corrected.

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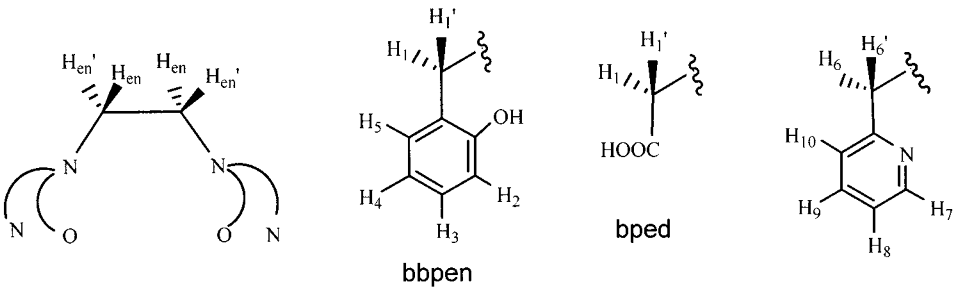
Table 1. ^1H NMR Data (200 MHz) for the Re(V) Complexes



assignment	$[ReO(H_2pmen)Cl_2]Cl{\cdot}CH_3OH^a$	$[ReO(bped)]Br^b$	$[ReO(bbpen)]PF_6$	$[ReO(Clbbpen)]PF_6$	$[ReO(bbpen)]_2[ReCl_6]^c$
H_{en}	3.32 (d, 2H)	3.65 (d, 2H)	3.61 (d, 2H)	3.65 (d, 2H)	3.40^d
H_{en}'	3.47 (d, 2H)	4.18 (d, 2H)	4.26 (d, 2H)	4.28 (d, 2H)	4.14 (d, 2H)
H_1		3.65 (d, 2H)	3.80 (d, 2H)	3.83 (d, 2H)	3.75 (d, 2H)
H_1'		3.77 (d, 2H)	4.63 (d, 2H)	4.64 (d, 2H)	4.52 (m, 2H)
H_2			6.31 (d, 2H)	6.34 (d, 2H)	6.32 (m, 2H)
H_3			6.95 (td, 2H)	6.96 (dd, 2H)	6.97 (t, 2H)
H_4			6.31 (t, 2H)		6.32 (m, 2H)
H_5			6.44 (d, 2H)	6.48 (d, 2H)	6.42 (d, 2H)
H_6	4.46 (d, 2H)	4.50 (d, 2H)	4.51 (d, 2H)	4.54 (d, 2H)	4.52 (m, 2H)
H_6'	4.88 (d, 2H)	5.22 (d, 2H)	5.36 (d, 2H)	5.33 (d, 2H)	5.12 (d, 2H)
H_7	8.89 (d, 2H)	9.12 (d, 2H)	8.17 (d, 2H)	8.23 (d, 2H)	8.11 (d, 2H)
H_8	7.55−7.7 (m)	7.6−7.8 (m)	7.16 (t, 2H)	7.26 (td, 2H)	7.21 (t, 2H)
H_9	7.93 (td, 2H)	8.03 (td, 2H)	7.82 (td, 2H)	7.90 (td, 2H)	7.85 (t, 2H)
H_{10}	7.55−7.7 (m)	7.6−7.8 (m)	7.61 (d, 2H)	7.65 (d, 2H)	7.57, (d, 2H)

[a] $CD_3OD/D_2O/DCl$. [b] CD_3OD. [c] DMSO-d_6. [d] This signal overlaps with residual water protons in the solvent.

obtained from Aldrich or Alfa and used without further purification. *N,N'*-Bis(salicylidene)ethylenediamine (H_2salen),[17] *N,N'*-bis(2-hydroxybenzyl)ethylenediamine (H_2bben),[18] *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)ethylenediamine (H_2bbpen),[18] *N,N'*-bis(5-chloro-2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)ethylenediamine (H_2Clbbpen)[18] and *N,N'*-bis(2-pyridylmethyl)ethylenediamine-*N,N'*-diacetic acid dihydrochloride ($H_2bped{\cdot}2HCl$)[19] were prepared as previously described in the literature. $[ReOCl_3(PPh_3)_2]$,[20] $K_2[ReCl_6]$,[21] and $[(C_4H_9)_4N][ReOBr_4]$[22] were synthesized by literature methods.

Instrumentation. IR (infrared) spectra were recorded as KBr disks in the range 4000−500 cm^{-1} on a Mattson Galaxy Series 5000 FTIR spectrophotometer. Mass spectra (Cs^+, LSIMS (liquid secondary ion mass spectrometry)) were obtained on a Kratos Concept II H32Q with thioglycerol as the matrix. In one complex ($[ReO(bbpen)]_2[ReCl_6]$), mass spectra were obtained in both positive and negative ion detection modes. C, H, N, and Cl analyses were performed by Mr. Peter Borda in this department. NMR spectra were recorded on a Bruker AC-200E (^1H, $^1H-^1H$ COSY) spectrometer and are reported as δ in ppm from external TMS (see Table 1).

Synthesis of *N,N'*-Bis(2-pyridylmethyl)ethylenediamine Tetrahydrochloride ($H_2pmen{\cdot}4HCl$). This was prepared by a variation on a literature method.[23] To a methanol (30 mL) solution of ethylenediamine (5.39 g, 89.8 mmol) and 2-pyridine carboxaldehyde (20.27 g, 189 mmol) was added sodium borohydride (8.49 g, 224 mmol), producing vigorous exothermic effervescence. After 2 h, the solvent was removed under reduced pressure and the resultant yellow solid was dissolved in 10% NH_4Cl (90 mL). The crude product was extracted with chloroform (3 × 75 mL), and the combined fractions were dried ($MgSO_4$). The solvent was removed, and the yellow oil was dissolved in a minimum amount of ethanol. A white precipitate was produced when 12 M HCl was added to the ethanol solution, and the precipitate was collected by suction filtration. Anal. Calcd (found) for $H_2pmen{\cdot}4HCl$ ($C_{14}H_{22}N_4Cl_4$): C, 43.32 (43.50); H, 5.71 (6.00); N, 14.43 (14.09). Mass spectrum (+LSIMS): $m/z = 243$ ($[C_{14}H_{19}N_4]^+$).

$[ReOCl_2(H_2pmen)]Cl{\cdot}CH_3OH$. $[NH_4][ReO_4]$ (52 mg, 0.20 mmol) and $H_2pmen{\cdot}4HCl$ (78 mg, 0.20 mmol) were suspended in methanol (10 mL) with heating. Triphenylphosphine (52 mg, 0.20 mmol) was added to the suspension, and the mixture was heated at 70 °C for 1 h, resulting in a brown solution. Diethyl ether (~15 mL) was added until the solution turned slightly turbid, and the mixture was kept at −10 °C over a few days, over which time yellow crystals precipitated. Anal. Calcd (found) for $[ReOCl_2(H_2pmen)]Cl{\cdot}CH_3OH$ ($C_{15}H_{22}Cl_3N_4O_2Re$): C, 30.91 (30.86); H, 3.80 (3.75); N, 9.61 (9.67). Mass spectrum (LSIMS): $m/z = 515$ ($[ReOCl_2(H_2pmen)]^+$), 443 ($[ReO(C_{14}H_{16}N_4)]^+$). IR (cm^{-1}, KBr disk): 927 ($\nu_{Re=O}$). The crystals were dissolved in methanol with a drop of concentrated HCl; diethyl ether was allowed to diffuse into the mixture, and single crystals of $[ReOCl_2(H_2pmen)]Cl{\cdot}2CH_3OH$ precipitated in a day or two. (Detailed chemistry of Re with the pmen ligand will be published elsewhere.[24])

$[ReO(bped)]Br{\cdot}H_2O$. To a refluxing solution of $H_2bped{\cdot}2HCl$ (60 mg, 0.14 mmol) in 10 mL of a methanol/ethanol (2:3) mixture was added sodium acetate (77 mg, 0.57 mmol) to produce a clear pale yellow solution. The solution was refluxed for 10 min, and a red acetonitrile solution (3 mL) of $[Bu_4N][ReOBr_4]$ (100 mg, 0.131 mmol) was added dropwise to give a clear green solution. Refluxing was continued for 30 min, and the solution was then stirred for 2 days at room temperature. A gray solid was recovered by filtration and recrystallized from ethanol. Anal. Calcd (found) for $[ReO(bped)]Br{\cdot}H_2O$ ($C_{18}H_{22}BrN_4O_5Re$): C, 33.11 (32.93); H, 3.70 (3.38); N, 8.25 (8.53). Mass spectrum (LSIMS): $m/z = 559$ ($[ReO(bped)]^+$), 443 ($[ReO(C_{14}H_{16}N_4)]^+$). IR (cm^{-1}, KBr disk): 923 ($\nu_{Re=O}$).

$[ReO(bped)]ReO_4{\cdot}H_2O$. $H_2bped{\cdot}2HCl$ (20 mg, 0.035 mmol) and $[NH_4][ReO_4]$ (11 mg, 0.039 mmol) were dissolved in 2 mL of ethanol. Triphenylphosphine (13 mg, 0.050 mmol) was added, and a gray precipitate was produced. The mixture was heated for 30 min, and another portion of NH_4ReO_4 (14 mg, 0.050 mmol) was dissolved with heating. The supernatant was decanted off, and the gray solid was washed with ethanol and dried under vacuum. Anal. Calcd (found) for $[ReO(bped)]\ [ReO_4]{\cdot}H_2O$ ($C_{18}H_{22}N_4O_{10}Re_2$): C, 26.15 (26.29); H, 2.68 (2.77); N, 6.78 (6.41). IR (cm^{-1}, KBr disk): 920 ($\nu_{Re=O}$). Single crystals

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Table 2. Selected Crystallographic Data

complex	$[ReO(H_2pmen)Cl_2]Cl{\cdot}2CH_3OH$	$[ReO(bped)][ReO_4]{\cdot}CH_3OH$	$[ReO(bbpen)]PF_6$
formula	$C_{16}H_{26}Cl_3N_4O_3Re$	$C_{19}H_{24}N_4O_{10}Re_2$	$C_{28}H_{28}F_6N_4O_3PRe$
fw	614.96	840.82	799.71
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pca2_1$	$P2/c$
a, Å	7.3495(4)	23.031(1)	11.9219(4)
b, Å	13.7679(8)	8.7674(4)	10.1817(4)
c, Å	20.492(2)	23.126(1)	12.7269(4)
β, deg	90.227(8)		111.001(1)
V, Å^3	2073.5(2)	4669.6(4)	1442.24(9)
Z	4	8	2
ρ_{calc}, g/cm^3	1.970	2.392	1.842
T, °C	−100(2)	−100(2)	−100(2)
radiation	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.71073	0.71073	0.71073
μ, cm^{-1}	62.72	104.23	43.45
transm factor	0.382−0.602	0.416−0.814	0.289−0.671
R^a	0.0253	0.0304	0.0186
wR2^a	0.0571	0.0679	0.0505
final shift/esd max	0.004	0.001	0.002

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) in the Three Complex Cations

	$[ReO(H_2pmen)Cl_2]^+$	$[ReO(bped)]^{+\,d}$	$[ReO(bbpen)]^+$
Re−O(oxo)	1.682(3)	1.689(4)/1.687(4)	1.689(3)
Re−N(amine 1)	2.310(3)	2.320(4)/2.319(4)	2.363(2)
Re−N(amine 2)	2.286(3)	2.320(4)/2.320(4)	2.363(2)
Re−X(1)$^{a-c}$	2.361(1)^c	2.014(4)/2.012(3)^b	2.002(2)^{a,b}
Re−X(2)$^{a-c}$	2.356(1)^c	2.017(5)/2.020(4)^b	2.002(2)^{a,b}
Re−N(pyridine 1)^a	2.247(3)	2.232(4)/2.232(4)	2.257(2)
Re−N(pyridine 2)^a	2.254(3)	2.228(4)/2.227(4)	2.257(2)
X(1)−Re−O(oxo)^a	98.5(1)	102.8(2)/102.4(2)	101.73(6)
X(2)−Re−O(oxo)	99.3(1)	101.3(2)/101.4(3)	101.73(6)
X(1)−Re−X(2)	162.25(4)	155.9(2)/156.1(2)	156.5(1)
O(oxo)−Re−N(py1)	77.2(1)	80.1(2)/79.9(2)	76.40(6)
O(oxo)−Re−N(py2)	77.7(1)	80.5(2)/80.7(2)	76.40(6)
N(am1)−Re−N(py1)	67.7(1)	68.4(1)/68.3(2)	67.38(8)
N(am2)−Re−N(py2)	67.5(1)	68.4(2)/68.5(2)	67.38(8)
N(am1)−Re−N(am2)	70.0(1)	73.2(2)/73.0(2)	72.8(1)

[a] Symmetry operation used to generate equivalent atoms: $-x + 1, y, -z + ^1/_2$. [b] X = O. [c] X = Cl. [d] Two unique molecules per asymmetric unit.

suitable for X-ray diffraction studies were grown from a methanol solution as $[ReO(bped)][ReO_4]{\cdot}CH_3OH$.

$[ReO(bbpen)]PF_6$. H_2bbpen (93 mg, 0.20 mmol) was mixed with 50 μL of 8 M NaOH (0.4 mmol) in 5 mL of methanol. This solution was then added to a 5 mL suspension of $ReOCl_3(PPh_3)_2$ (170 mg, 0.21 mmol) in methanol, and the mixture was refluxed for 1.5 h. The resultant brown solution was cooled to room temperature, and $NaPF_6$ (35 mg, 0.21 mmol) was added. The mixture was left at room temperature for slow evaporation over a 3 day period; the resulting light red precipitate was collected by filtration from the dark greenish brown filtrate, yield 35 mg (22%). Anal. Calcd (found) for $[ReO(bbpen)]PF_6{\cdot}0.5H_2O$ ($C_{28}H_{29}F_6N_4O_{3.5}PRe$): C, 41.58 (41.53); H, 3.61 (3.43); N, 6.93 (6.60). Mass spectrum (LSIMS): $m/z = 655$ ($[ReO(bbpen)]^+$), 443 ($[ReO(C_{14}H_{16}N_4)]^+$). IR (cm^{-1}, KBr disk): 946 ($\nu_{Re=O}$). Crystals suitable for X-ray diffraction studies were grown from CH_3CN/methanol.

$[ReO(Clbbpen)]PF_6{\cdot}H_2O$. A procedure similar to that for the $[ReO(bbpen)]PF_6$ synthesis was followed using H_2Clbbpen (110 mg, 0.21 mmol). The same workup yielded 38 mg of $[ReO(Clbbpen)]PF_6$ (22%). Anal. Calcd (found) for $[ReO(Clbbpen)]PF_6{\cdot}H_2O$ ($C_{28}H_{28}Cl_2F_6N_4O_4PRe$): C, 37.93 (38.14); H, 3.18 (3.18); N, 6.32 (6.21). Mass spectrum (LSIMS): $m/z = 723$ ($[ReO(Clbbpen)]^+$), 443 ($[ReO(C_{14}H_{16}N_4)]^+$). IR (cm^{-1}, KBr disk): 949 ($\nu_{Re=O}$).

$[ReO(bbpen)]_2[ReCl_6]$. To a 5 mL methanolic suspension of $K_2[ReCl_6]$ (95 mg, 0.20 mmol) was added a mixture of H_2bbpen (94 mg, 0.21 mmol) and 8 M NaOH (50 μL, 0.4 mmol) in 5 mL of methanol. The mixture was refluxed for 23 h. After cooling to room temperature, the solution was filtered. The brown product was collected, washed with water and then Et_2O, and dried in air, yield 38 mg (40%). Anal. Calcd (found) for $[ReO(bbpen)]_2[ReCl_6]{\cdot}3H_2O$ ($C_{56}H_{62}Cl_6N_8O_9Re_3$): C, 38.16 (38.03); H, 3.55 (3.29); N, 6.36 (6.47); Cl, 12.07 (12.37). Mass spectrum (LSIMS): $m/z = 655$ ($[ReO(bbpen)]^+$), 443 ($[ReO(C_{14}H_{16}N_4)]^+$), 364$[ReCl_5]^-$. IR (cm^{-1}, KBr disk): 946 ($\nu_{Re=O}$).

X-ray Crystallographic Analyses. All crystal structure determinations were completed at the University of Minnesota. Selected crystallographic data are presented in Table 2. All specimens were mounted on glass fibers at −100 °C for individual data collections on a Bruker SMART platform diffractometer. Initial cell constants were determined from reflections extracted from 3 sets of 20 frames for each specimen. Final cell constants were calculated from a large set of strong reflections for each structure. The space group of each was determined on the basis of systematic absences and intensity statistics.[25] Each structure was solved by direct methods, which provided all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms. The isotropic displacements of the hydrogen atoms were also defined as riding on a function of the calculated isotropic displacements from the respective bonded atoms. Selected bond distances and angles appear in Table 3.

The space group for $[ReOCl_2(H_2pmen)]Cl{\cdot}2CH_3OH$ is $P2_1/n$. The chlorine anion is coordinated by a hydrogen bond from each methanol and by two amine protons from the H_2pmen ligand. The space group for $[ReO(bped)][ReO_4]{\cdot}CH_3OH$ is $Pca2_1$; however, there are two

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(25) *SHELXTL-Plus*, version 5.4; Siemens Industrial Automation, Inc.: Madison, WI, 1999.

formula equivalents in the asymmetric unit. This structure is problematic because the contents appear to have a pseudo inversion center (local center) in an otherwise polar space group.[26] The presence of the local center causes an unstable least-squares refinement.[27] Bond distances and angles and anisotropic displacement parameters are adversely affected. To this end, restraints were applied to steer the refinement toward a chemically reasonable result. The C_2 symmetry of the [ReO(bped)]$^+$ group was advantageous in the application of these restraints. The pair of [ReO(bped)]$^+$ groups are strongly related by the local center. One of the two $[ReO_4]^-$ groups is disordered. Each methanol solvent is hydrogen bonded to a $[ReO_4]^-$ group. The similarity of the *a* and *c* axes indicated a need to check for possible pseudomerohedral twinning. None was found; however, there was a small component of inversion twinning present. Several large peaks remained in difference Fourier maps after the initial refinement was complete with peaks ca. 2.5 e Å^{-3}. One of these was close to O(3). The proximity of this feature required the application of an anisotropic displacement parameter restraint. The space group for [ReO(bbpen)]PF_6 is *P*2/*c*.

Complete tables of crystallographic data, atomic coordinates with equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters, torsion angles, hydrogen coordinates and isotropic displacement parameters, and hydrogen bond lengths and angles are available as Supporting Information.

Results and Discussion

A few different synthetic routes were used to prepare the monocationic $Re^{V}{=}O$ complexes. $[Re^{V}O(L)]^+$ (L = bbpen and Clbbpen) were synthesized from two different starting materials: $Re^{V}OCl_3(PPh_3)_2$ and $K_2[Re^{IV}Cl]_6$. The substitution reaction of $Re^{V}OCl_3(PPh_3)_2$ with the ligands premixed with NaOH in the presence of $NaPF_6$ in methanol at reflux temperature resulted in complexes with PF_6^- as the counteranion. The reaction with $K_2[Re^{IV}Cl]_6$ as a starting material involved the facile aerial oxidation of Re(IV) to Re(V), and the resulting monocationic complexes precipitated as $[Re^{V}O(L)]_2[ReCl_6]$. A metathesis reaction of $[(n\text{-}C_4H_9)_4N][ReOBr_4]$ with H_2bped·HCl produced an immediate precipitate ([ReO(bped)]Br) in high yield. Alternatively, [ReO(bped)]$[ReO_4]$ can be synthesized by reducing $[NH_4][ReO_4]$ with triphenylphosphine in the presence of the ligand, as was done in the case of $[ReOCl_2(H_2pmen)]Cl\cdot CH_3OH$. While bulk synthesis of $[ReOCl_2(H_2pmen)]Cl\cdot CH_3OH$ resulted in microcrystalline material with one methanol solvate, single crystals of the material contained two lattice methanol molecules.

All complexes were characterized by IR, mass spectrometry, elemental analysis,^{1}H NMR, and, in the cases of [ReO(bbpen)]PF_6, [ReO(bped)]$[ReO_4]\cdot CH_3OH$, and $[ReO(H_2pmen)Cl_2]Cl\cdot 2CH_3OH$, by X-ray crystal structure analysis. The infrared stretching vibrations $\nu_{Re=O}$ of the cationic complexes [ReO(bbpen)]PF_6, [ReO(bped)]$[ReO_4]$, and $[ReO(H_2pmen)Cl_2]Cl\cdot CH_3OH$ were found to be 946, 920, and 927 cm^{-1}, respectively. The values are typical of $Re^{V}{=}O$ complexes with the latter two at the lower end of the reported values.[15,28] In the mass spectra of all the complexes, M$^+$ parent peaks were observed. Another predominant peak present in all the complexes is that of the $[ReO(C_{14}H_{16}N_4)]^+$ fragment, indicative of the loss of two apical pendent arms of the ligands for [ReO(bbpen)]$^+$ and [ReO(bped)]$^+$, and of loss of two HCl for $[ReO(H_2pmen)Cl_2]^+$. This fragmentation is also detected in lanthanide (Ln(III))[29] and Fe(III)[30] complexes with bbpen^{2-}. The presence of the $[ReCl_6]^{-2}$

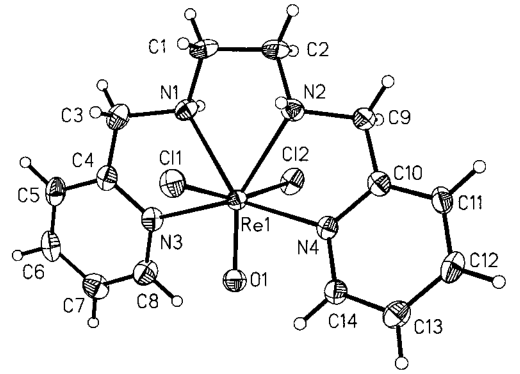

Figure 1. Thermal ellipsoid drawing of the $[ReO(H_2pmen)Cl_2]^+$ cation in $[ReO(H_2pmen)Cl_2]Cl\cdot 2CH_3OH$ showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

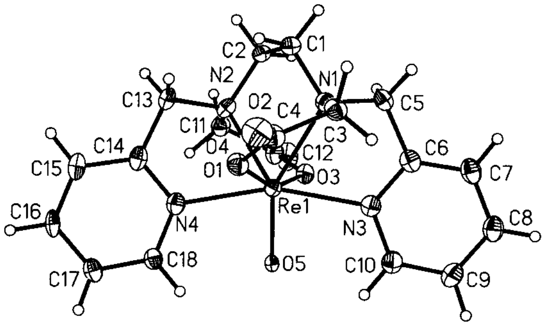

Figure 2. Thermal ellipsoid drawing of the [ReO(bped)]$^+$ cation in [ReO(bped)]$[ReO_4]$ showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

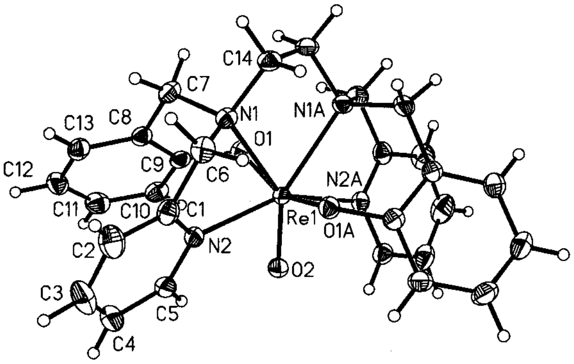

Figure 3. Thermal ellipsoid drawing of the [ReO(bbpen)]$^+$ cation in [ReO(bbpen)]PF_6 showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

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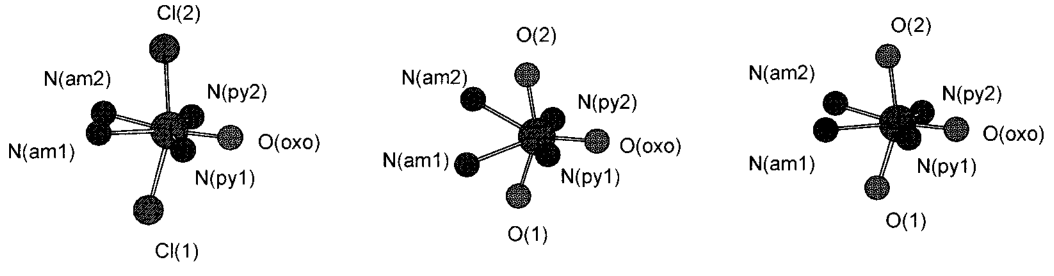
(26) Marsh, R. E.; Shoemaker, V.; Herbstein, F. H. *Acta Crystallogr., Sect. B* **1998**, *54*, 921.

(27) The two cations, anions, and solvents in the asymmetric unit are related by a surprisingly exact center of inversion near $x = {}^7/_8$, $y = {}^1/_4$. In this situation large correlations are expected in the least-squares refinement. Many different restraint/constraint models were tested prior to settling on the one reported here. The presence of the local center forced the usage of a restraint/constraint model that maintained similar 1,2 and 1,3 bond distances for pseudosymmetrically related groups in the cation, as well as those that were related by a noncrystallographic C_2. Anisotropic displacement parameters of neighboring atoms were restrained to have similar values as well. Likewise, the anions were refined with similar restraints for positional parameters, but the anisotropic displacement parameters were restrained to approximate rigid group motion. Anisotropic displacement parameters of the solvent were restrained similarly. Release of any of these restraints diminished the chemical reasonableness of the result, *in particular, the bond lengths and angles*. Accordingly, the addition of the restraints has *artificially lowered* all esd values for bond distances and bond angles by at least a factor of 2. The application of restraints has necessarily averaged bond distances and bond angles, and those values should be viewed as such.

(28) Botha, J. M.; Umakoshi, K.; Sasaki, Y.; Lamprecht, G. J. *Inorg. Chem.* **1998**, *37*, 1609.



$[ReO(H_2pmen)Cl_2]^+$ $[ReO(bped)]^+$ $[ReO(bbpen)]^+$

Figure 4. Drawing of the coordinating atoms in the $[ReO(H_2pmen)Cl_2]^+$, $[ReO(bped)]^+$, and $[ReO(bbpen)]^+$ cations.

counteranion in $[ReO(bbpen)]_2[ReCl_6]$ was confirmed by negative mode LSIMS and was consistent with the elemental analysis.

Suitable crystals for X-ray crystallographic analysis were grown for $[ReO(bbpen)]PF_6$ (from an acetonitrile/methanol mixture), $[ReO(bped)][ReO_4]\cdot CH_3OH$ (from methanol), and $[ReO(H_2pmen)Cl_2]Cl\cdot 2CH_3OH$ (from methanol/diethyl ether). The structures of the complex cations are remarkably similar (Figures 1−4); along with a reported complex $[ReO(qtp)(OCH_3)_2]ClO_4$,[9] we believe, they represent a unique structural motif in $Re^V{=}O$ chemistry. All three metal complexes are C_2 symmetric; the rhenium center in all the complexes is seven-coordinate with a rarely observed distorted pentagonal bipyramidal geometry. The rhenium atom sits in a basal plane formed by an oxo O and four N atoms. The basal planarity indicates the degree of strain imposed by axial ligand linkage to the ethylenediamine backbone. Specifically, the basal plane of $[ReO(H_2pmen)Cl_2]^+$ is almost perfectly planar; that of [ReO(bbpen)] is slightly skewed; and that of [ReO(bped)] is significantly distorted, most likely by chelation of NCH_2COO^- units forming five-membered rings (Figure 4). This planarity of the basal plane is also observed in $[ReO(qtp)(OCH_3)_2]ClO_4$, in which the axial methoxide ligands are not linked to the basal N_4 unit. The basal pentagon is distorted, possibly to accommodate the Re═O linkage: N(py)−Re−O(oxo) angles range from 76.40(6)° to 80.67(17)°, which pinch the N−Re−N angles (67−72°) from the ideal value of 72°. This is also mirrored in $[ReO(qtp)(OCH_3)_2]ClO_4$ (in which N(py)−Re−O(oxo) ~ 77.3° and N−Re−N ~ 68.5°).[9]

In all three structures, the two axial atoms are bent away from the oxo (O(axial)−Re−O(oxo) ~ 102° and Cl−Re−O(oxo) ~ 99°, as opposed to 90° in an ideal pentagonal bipyramid). The degree of bending seems to be unaffected by the strain imposed by the linkage of the axial atoms to the basal unit, as verified by the strain-free $[ReO(qtp)(OCH_3)_2]ClO_4$ structure (O(axial)−Re−O(oxo) = 101.5(2)°);[9] and the axial coordinating atoms do not significantly change the bending as there is <3° from Cl to O ligands. The two axial atoms, oxo O, and Re form an axial plane bisecting the molecule. The axial plane is perpendicular to the basal plane in $[ReO(H_2pmen)Cl_2]^+$ (and $[ReO(qtp)(OCH_3)_2]^+$) without the ligand-imposed strain; otherwise it tilts, slightly in $[ReO(bbpen)]^+$ and significantly in $[ReO(bped)]^+$.

The Re═O bond lengths in the three complex cations are almost identical, verifying the remarkable similarity of the three complexes.[28,31] The Re−N(pyridine) bonds are within the range of typical Re−N bonds (2.10−2.27 Å in Re^VO complexes),[28,32] whereas the Re−N(amine) bonds exceed this range, probably because they are trans to the oxo group. The Re−O(axial) distances (~2.00 Å) of the two relevant complexes are only slightly different and are comparable to those in $[ReO(qtp)(OCH_3)_2]^+$ (~1.98 Å).[9] This lack of variance in the axial bond lengths, along with the observation that the O−Re−O(axial) bond angle remains the same in all the complexes, suggests that the axial ligands are hardly affected by the rest of the molecule.

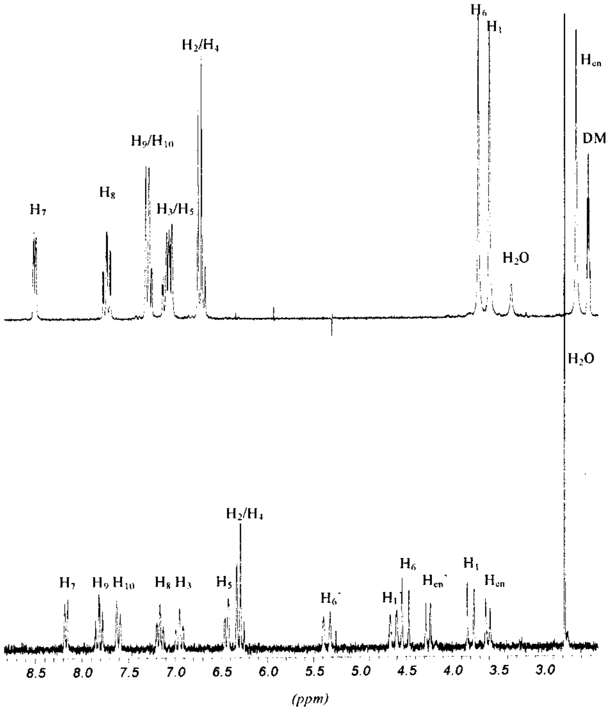


Figure 5. ^1H NMR spectra of H_2bbpen, in DMSO-d_6 (top), and of $[ReO(bbpen)]PF_6$ in acetone-d_6 (bottom).

The similarities of these complexes warrant a generalization of some interesting and, indeed, surprising features of their structures. (1) The complexes all have pentagonal bipyramidal geometries with an oxo O and four neutral N atoms in the basal plane; given the spatial and electronic demands of an oxo group, one hardly expects to find it in the cluttered basal plane. (2) Without ligand-imposed strain, the basal plane is perfectly planar. (3) The anionic ligands occupy the axial positions, which are distorted away from the oxo group, and the degree of bending does not seem to be affected by the nature of the ligands or the rest of the molecule. (4) The oxo O, the Re, and the axial ligands form an axial plane bisecting the molecule.

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(29) Setyawati, I. A.; Liu, S.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **2000**, *39*, 496.

(30) Setyawati, I. A.; Rettig, S. J.; Orvig, C. *Can. J. Chem.* **1999**, *77*, 2033.

(31) Rouschias, G. *Chem. Rev.* **1974**, *74*, 531.

(32) Lock, C. J. L.; Turner, G. *Acta Crystallogr. Sect. B* **1978**, *34*, 923.

^{1}H NMR spectroscopy indicates that under suitable conditions all three cations retain their solid state structures in solution. The assignments of all protons in all the complexes are presented in Table 1. As an example, spectra of H_2bbpen and [ReO(bbpen)]$^+$ are shown in Figure 5; similar structural features in solution were observed by ^{1}H NMR spectroscopy for the [ReO(H_2pmen)Cl_2]$^+$ and [ReO(bped)]$^+$ cations. Crystallographic data indicate that all three complex cations are C_2 symmetric. This feature is echoed in their ^{1}H NMR spectra: proton signals of ethylene, methylene adjacent to the pyridine, and the methylene of the pendent arms of the [ReOL]$^+$ cations split into two sets of doublets with coupling constants consistent with geminal coupling. Also, there is only one set of pyridine (and oxobenzene in [ReO(bbpen)]$^+$) H resonances. Curiously, the chemical shifts of the pyridine H resonances in [ReO(bbpen)]$^+$ are lower than those in [ReO(bped)]$^+$ and [ReO(H_2pmen)Cl_2]$^+$; one is tempted to speculate about the shielding effects of the nearby phenolates. Minor differences aside, the fact that all the complexes retain the seven-coordinate structure in solution suggests that they are robust and that the structural motif they represent is potentially general.

Conclusions

The oxorhenium(V) complexes with H_2pmen, H_2bbpen and H_2Clbbpen, and H_2bped have been synthesized. X-ray crystallographic analyses of the [ReO(H_2pmen)Cl_2]$^+$, [ReO(bbpen)]$^+$, and [ReO(bped)]$^+$ complexes showed that all three cations share a rare seven-coordinate structure with a distorted pentagonal bipyramidal geometry, which represents a novel, and potentially general, structural motif in $Re^{V}{=}O$ complexes. The solution structures of the complexes are similar to those in the solid state, as confirmed by the ^{1}H NMR spectra.

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Supporting Information Available: ^{1}H$-^1$H COSY spectrum of [ReO(bbpen)]PF_6 in acetone-d_6. For all the structures, complete tables of crystallographic data, atomic coordinates with equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters, torsion angles, hydrogen coordinates and isotropic displacement parameters, and hydrogen bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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