2166 *Inorg. Chem.* **1997,** *36,* 2166−2169

Tungstorhenate Heteropolyanions. 2. Synthesis and Characterization of Enneatungstorhenates(V), -(VI), and -(VII)[†]

Fernando Ortéga, Michael T. Pope,* and Howard T. Evans, Jr.[‡]

Department of Chemistry, Georgetown University, Washington, D.C. 20057

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The tungstorhenate(V) heteropolyanion $[W_9ReO_{32}]^{5-}$ has been isolated as guanidinium and cesium salts from reaction of $[ReO_2(PPh_3)(py)_3]^+$ with sodium tungstate. Crystallographic analysis of black $Cs_5[W_9ReO_{32}]\cdot 3H_2O$ [triclinic, $P1$ or $P\bar{1}$; $a = 10.194(1)$, $b = 11.503(2)$, $c = 9.682(1)$ Å; $\alpha = 100.55(1)$, $\beta = 115.81(1)$, $\gamma = 99.13(1)°$; $Z = 1$], based on 3743 reflections, shows the anion to be isostructural with decatungstate, $[W_{10}O_{32}]^{4-}$. Refinement in $P\bar{1}$ led to reliability indices $R = 0.084$, $R_w = 0.046$. Electrochemical investigation revealed the existence of Re^{VI} and Re^{VII} analogues, which were hydrolytically unstable in aqueous solution but which were isolated as crystalline tetra-*n*-butylammonium and tetra-*n*-heptylammonium salts, respectively, from nonaqueous solvents. The tetra-*n*-butylammonium salts of $[W_9Re^{VI}O_{32}]^{4-}$ and $[W_{10}O_{32}]^{4-}$ were shown to be isomorphous by X-ray powder diffraction. Simulation of the Q-band ESR spectrum of $[W_9Re^{VI}O_{32}]^{4-}$ (polycrystalline solid solution in $[W_{10}O_{32}]^{4-}$) gave $g_x = 1.69(1)$, $g_y = 1.66(1)$, $g_z = 1.730(2)$ and $10^4A_x(^{185,187}Re, I = {}^5/_2) = (-)252(10)$, $10^4A_y = (-)398(10)$, $10^4A_z = (-)653(5)$ cm^{-1}. The orthorhombic ESR spectrum proves that the Re atom occupies one of the eight equivalent "equatorial" sites in the decatungstate structure.

Interest in the chemistry of heteropoly oxometalate anions has increased enormously in the past few years.[1] This can probably be traced to the potential applications of polyanions in thermo- and photocatalysis, in biochemistry and medicine, and also to the broader availability of powerful new experimental methods (notably multinuclear NMR) that can complement X-ray crystallography for structural investigations. The major polyoxoanion-forming elements are W^{6+}, Mo^{6+} and V^{5+} for reasons that are well understood, namely ionic radii that favor four-, five-, and six-coordination by the oxide ion and availability of orbitals that can participate in π-bonding with oxygen.[2] Neighboring elements, Nb^{5+}, Ta^{5+}, and Re^{7+}, are also appropriate, and indeed a limited number of polyanions incorporating these are known. Several years ago we reported the first structurally-characterized polyanions to contain rhenium atoms.[3] These species were heteropolytungstates with the familiar Keggin structure in which one or two tungsten atoms had been replaced by rhenium. The polyanions showed a remarkable electrochemistry in which all rhenium oxidation states between 3 and 7 could be accessed. We have also investigated possibilities for tungstorhenate polyanions other than those derived from lacunary polytungstates. In the present paper, we report one such species which proves to have a structure based upon the isopoly decatungstate anion.

Experimental Section

Syntheses. Oxotribromobis(triphenylphosphine)rhenium(V), $[ReOBr_3(PPh_3)_2]$, was prepared according to the literature.[4]

Dioxotris(pyridine)(triphenylphosphine)rhenium(V) Bromide, $[ReO_2(PPh_3)(C_5H_5N)_3]Br\cdot 2H_2O$. One milliliter of pyridine was added to a suspension of 3.0 g of $[ReOBr_3(PPh_3)_2]$ in dichloromethane, and the mixture was stirred until the solid had dissolved (20 min). The resulting yellow-orange solution was refrigerated for 5−6 h, after which the orange crystals were removed by filtration and washed with acetone. Yield: 75%. Anal. Calcd (found): C, 47.52 (47.60); H, 4.07 (4.00); N, 5.04 (5.21); P, 3.72 (3.91).

Guanidinium 9-Tungstorhenate. A solution of 6.6 g (20 mmol) of Na_2WO_4 in 50 mL of water adjusted to pH 4.5−5 with acetic acid was mixed with a solution of 3.3 g (4 mmol) of $[ReO_2(PPh_3)(py)_3]Br\cdot 2H_2O$ in 40 mL of water−methanol (1:1). A precipitate appeared immediately upon mixing but mostly dissolved to give a purple solution when the mixture was heated to boiling. After boiling for a further 5 min, the solution was allowed to cool and was filtered. Ten grams of guanidinium hydrochloride was added to yield a purple precipitate, which was filtered off. The violet filtrate was placed in a refrigerator, and after 2 days about 1 g (*ca.* 15% yield based on tungsten) of small dark crystals was produced. These were recrystallized from water. Anal. Calcd (found) for $(CN_3H_6)_5[W_9ReO_{32}]\cdot 3H_2O$: C, 2.72 (2.50); H, 1.33 (1.35); N, 7.76 (7.75); W, 61.12 (61.21); Re, 6.88 (6.87); H_2O, 1.84 (1.87). Crystal data: monoclinic, $P2_1m$; $a = 15.231(2)$, $b = 12.203(1)$, $c = 11.211(1)$ Å; $\beta = 101.3°$.

Cesium 9-Tungstorhenate(V). Cesium chloride was stirred into a solution of 0.5 g of the guanidium salt in 10 mL of water until a precipitate appeared. The mixture was warmed to complete redissolution, and upon cooling, crystals of the desired salt were formed. Yield: 0.45 g (80%). Anal. Calcd (found) for $Cs_5[W_9ReO_{32}]\cdot 3H_2O$: Cs, 21.61 (18.67); W, 53.81 (53.61); Re, 6.07 (6.13); H_2O, 1.76 (1.80). Crystallographic work is described below.

Tetra-*n*-butylammonium 9-Tungstorhenate(VI). Fifty milliliters benzene was washed with 50 mL of 0.03 M NaBr prepared from freshly-distilled water. Two grams of tetra-*n*-heptylammonium bromide was dissolved in the benzene, and the solution was transferred to a separatory funnel containing 0.5 g of $(CN_3H_6)_5[W_9ReO_{32}]\cdot 3H_2O$ dissolved in 20 mL of water. After the mixture was shaken for 1 min, the (now colorless)

[†] From the Ph.D. thesis of F.O., Georgetown University, 1982.

[‡] U.S. Geological Survey, National Center 954, Reston, VA 20192.

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aqueous layer was discarded and the benzene layer transferred to a beaker, where it slowly changed color from violet to red-brown. Addition of a solution of 5 g of tetra-*n*-butylammonium bromide in 10 mL of methanol produced, after *ca.* 12 h, a dark precipitate that was filtered off and washed with methanol. The solid was dissolved in 10 mL of acetonitrile, 50 mL of methanol was added, and after 12−24 h a crystalline solid was obtained in virtually quantitative yield. Anal. Calcd (found) for $[(C_4H_9)_4N]_4[W_9ReO_{32}]$: C, 23.23 (23.71); H, 1.70 (1.95); N, 4.35 (4.56); W, 49.6 (49.4); Re, 5.60 (5.82). Crystal data: orthorhombic, *Pcab*; $a = 24.193(7)$, $b = 24.455(12)$, $c = 16.467(6)$ Å.

Tetra-*n*-heptylammonium 9-Tungstorhenate(VII). The benzene solution containing $[W_9ReO_{32}]^{4-}$ from the above procedure was allowed to evaporate to about 10 mL, and a few drops of bromine were added to cause a color change from red-brown to yellow. After the addition of 10 mL of methanol, the solution was placed in the refrigerator. Yellow crystals formed after 12−24 h. They were filtered off and washed with ether. Anal. Calcd (found) for $[(C_7H_{15})_4N]_3[W_9ReO_{32}]$: C, 28.13 (27.99); H, 5.02 (4.93); N, 1.17 (1.24); W, 46.18 (46.38); Re, 5.20 (5.48).

Physical Measurements and Structure Analysis. Electrochemical and spectroscopic measurements were carried out using instrumentation described earlier.[3] In order to confirm the presumed analogy of the $[W_9ReO_{32}]^{5-}$ complex to the well-known $[W_{10}O_{32}]^{4-}$ structure,[5] a structure analysis of $Cs_5[W_9ReO_{32}]\cdot 3H_2O$ was carried out. The black crystals (deep blue in thin flakes) are triclinic, forming lozenge-shaped plates, flattened on (010). The unit cell dimensions found by X-ray precession photography were refined by least-squares analysis using a set of 88 X-ray powder data obtained with a Guinier-Hagg focusing camera using Cr Kα_1 radiation ($\lambda = 2.289\,70$ Å). Intensity data were collected for one hemisphere in reciprocal space to $2\theta = 60°$ on a modified Picker automatic diffractometer. The unit cell contains one formula unit, but although the rhenium atom cannot lie on a symmetry center, the structure conforms closely to space group $P\bar{1}$. An electron density map obtained with a set of phases found by the symbolic addition procedure (using a preliminary data set of 1519 reflections confined to $2\theta < 40°$) immediately revealed the decatungstate-type molecule. Three Cs atom sites were located, one of which [Cs(3)] was found to be half-occupied by refinement of the population parameter. This confirms the stoichiometry of the salt in spite of a slightly low elemental analysis for Cs. Six water molecules [O(17)−O(22)] were located in the difference maps, all of which were found by refinement of the population parameters to be half-occupied. All attempts to refine the structure in the lower symmetry failed significantly to improve the goodness-of-fit; therefore, only the $P\bar{1}$ structure is reported. This situation, where 93% of the X-ray scattering power is nearly perfectly centrosymmetric, has been shown by Marsh[6] to be nonrefinable in the lower symmetry. Also, it is not possible to distinguish between W and Re (atomic numbers 74 and 75) in the X-ray experiment. Thus, the crystal structure analysis has served to establish the molecular structure but unfortunately does not permit the determination of the location and environmental details of the Re atom. This question is addressed by the spectroscopic study described below.

Crystallographic and refinement data, structure parameters, anisotropic and isotropic displacement parameters, W--O bond lengths, and various Cs--O and O···O distances are given in the Supporting Information. Tables of observed and calculated structure factors may be obtained from H.T.E.

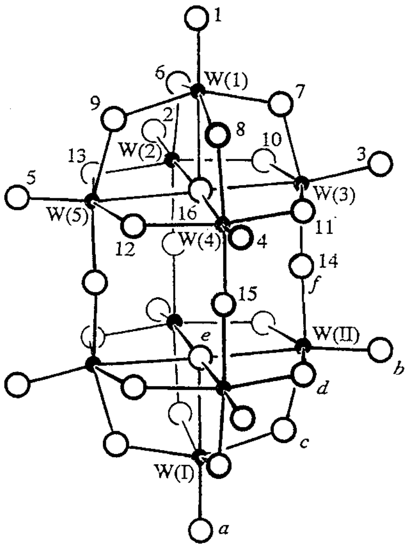

Figure 1. Diagram of the $[W_9ReO_{32}]^{5-}$ polyanion showing labeling of the atoms (above) and atom types (below) (numbers and letters only for O atoms). On the basis of spectroscopic evidence, the Re atom occupies one of the equivalent sites labeled II.

Table 1. Atomic Coordinates (Å) in the Symmetrized Model (4*mmm*) for $[W_9ReO_{32}]^{5-}$, with Averaged Distances and Angles

atom	*x*	*y*	*z*	*n*
W(I)	0	0	4.240	2
W(II)	2.320	0	1.891	8
O(a)	0	0	5.926	2
O(b)	3.993	0	2.100	8
O(c)	1.834	0	3.800	8
O(d)	1.851	1.851	1.836	8
O(e)	0	0	1.937	2
O(f)	2.252	0	0	4

	D (Å)		O--W--O (deg)
W(I)−O(a)	1.69	O(a)−O(c)	103.5
W(I)−O(c)	1.89	O(c)−O(c)	153.3
W(I)−O(d)	1.91	O(c)−O(c)	153.3
		O(c)−O(e)	76.6
W(II)−O(b)	1.69	O(b)−O(c)	97.2
W(II)−O(c)	1.97	O(b)−O(f)	99.2
W(II)−O(d)	1.91	O(b)−O(d)	104.1
W(II)−O(e)	2.32	O(e)−O(c)	74.6
W(II)−O(f)	1.92	O(e)−O(f)	89.1
		O(d)−O(e)	75.8
		O(d)−O(c)	86.7
		O(b)−O(e)	171.6
		O(c)−O(f)	163.6
		O(c)−O(c)	151.6

Figure 1 shows the atom numbering, as well as the atom type according to the averaged molecular symmetry (D_{4h}). Table 1 gives the Cartesian coordinates of the molecule averaged over the tetragonal symmetry 4*mmm*. In Table 2 the average lengths for each type of bond are shown and compared with those reported for $[W_{10}O_{32}]^{4-}$ by Fuchs *et al.*[5]

The programs used are contained in the XTAL86 system[7] and were implemented on a VZX780 computer and a SUN 4/110 workstation. Scattering factors, anomalous dispersion factors, and absorption coefficients were taken from Hamilton and Ibers.[8]

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Table 2. Average W--O Bonds in the Tetragonal $[W_9ReO_{32}]^{5-}$ and $[W_{10}O_{32}]^{4-}$ Polyanions

			dist (Å)			
atom	CN(O)[a]	n[b]	range	av	range[c]	av
W(I)						
−O(a)	1	1	1.68(2)[d]	1.68	1.76(3)[d]	1.76
−O(c)	2	4	1.83−1.94	1.89	1.84−1.95	1.90
−O(e)	5	1	2.30	2.30	2.32	2.32
av W(I)−O				1.92		1.95
W(II)						
−O(b)	1	4	1.62−1.74	1.69	1.68−1.71	1.70
−O(c)	2	4	1.93−2.01	1.97	1.98−2.06	2.02
−O(d)	2	8	1.86−1.97	1.91	1.88−1.93	1.91
−O(e)	5	4	2.29−2.34	2.32	2.27−2.33	2.30
−O(f)	2	4	1.85−1.93	1.89	1.85−1.95	1.90
av W(II)−O				1.95		1.96

[a] Coordination number of O to W. [b] Number of independent bonds. [c] From ref 5. [d] With typical esd.

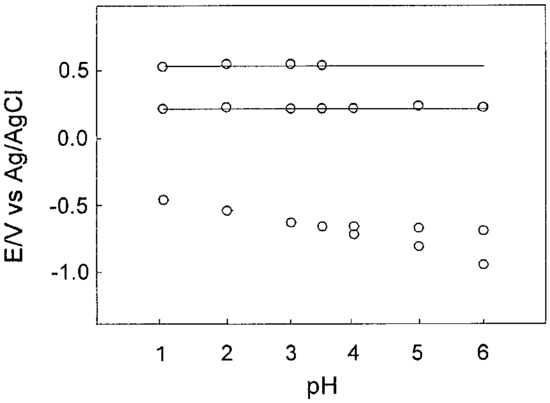

Figure 2. Variation of cathodic peak potentials with pH from cyclic voltammograms of aqueous solutions of $[W_9ReO_{32}]^{5-}$. Conditions: glassy carbon electrode; sweep rate 1.00 V min^{-1}.

Results and Discussion

The synthesis of $[W_9Re^{V}O_{32}]^{5-}$ from acidified tungstate and a particular pyridine−phosphine complex of Re(V), as described in the Experimental Section, is not particularly rational, nor are the yields good (*ca.* 15%). The anion is also formed when the tetrakis(pyridine) and bis(pyridine) bis(triphenylphosphine) complexes are used, but yields are much smaller. We were unable to discover other starting rhenium complexes that would provide an efficient entree into "binary" tungstorhenate polyanions.

Cyclic voltammetry of $[W_9ReO_{32}]^{5-}$ in aqueous solution showed two pH-independent quasireversible redox features at $E_{pc} = +0.55$ ($\Delta E_{pc/a} = 90$ mV) and +0.22 V ($\Delta = 60$ mV) *vs* Ag/AgCl, followed by a single irreversible ($\Delta = 170$ mV) pH-dependent peak that splits into two peaks at pH >4; see Figure 2. The two peaks at positive potential were assigned to $Re^{VI/VII}$ and $Re^{V/VI}$ couples, respectively, and the peaks at negative potentials probably correspond to tungsten reductions. The peak at 0.55 V was almost imperceptible at pH >4, although it was well defined when a high-voltage sweep rate was used. At potentials more negative than −1.0 V, an irreversible multielectron reduction was observed, with the oxidation step appearing at +0.35 V. This feature, observed in a number of Keggin 12-tungstates, may indicate the formation of a heteropoly "brown" with a W^{IV}_3 cluster unit.[9]

Controlled-potential oxidation at +0.45 V in order to generate the Re^{VI} species always resulted in a bleaching of the solution and loss of the characteristic voltammogram, indicating anion decomposition. Reduction at −0.70 V of a solution at pH 5 (acetate buffer) led to the stoichiometric addition of one electron and a color change from violet to blue. During the course of the reduction, the cyclic voltammogram deteriorated, and after aerial reoxidation of the blue solution, the visible spectrum indicated that only 30% of the starting material remained.

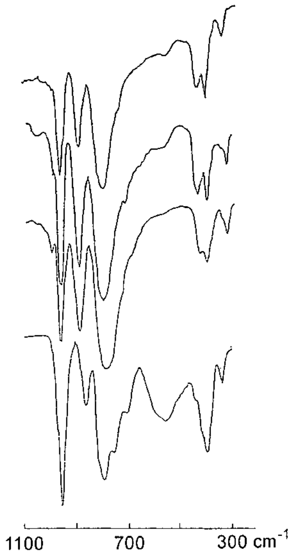

Figure 3. IR spectra of (top to bottom) $[W_9Re^{VI}O_{32}]^{4-}$, $[W_9Re^{VII}O_{32}]^{3-}$, $[W_{10}O_{32}]^{4-}$, and $[W_9Re^{V}O_{32}]^{5-}$.

The tetra-*n*-butylammonium salt of the Re^{VI} derivative is soluble in acetonitrile, dimethylformamide, dimethyl sulfoxide, and acetone. In these solvents it is indefinitely stable. In acetonitrile the cyclic voltammogram of $[W_9Re^{VI}O_{32}]^{4-}$ shows three reversible ($\Delta E_{pc/a} = 80$ mV) one-electron features with cathodic peak potentials of +0.32, −0.46, and −1.70 V and cathodic−anodic peak separations of 80 mV. Oxidation at +0.6 V led to almost stoichiometric (94%) removal of one electron and to a yellow solution of the Re^{VII} derivative. Reduction of the latter solution at −0.6 V restored the Re^{VI} species. Further reduction at −2.0 V could not be completed.

The vibrational spectra of $[W_9Re^{VI}O_{32}]^{4-}$, $[W_9Re^{VII}O_{32}]^{3-}$, and $[W_{10}O_{32}]^{4-}$ are virtually indistinguishable in the metal−oxygen stretching region, with three strong, relatively narrow bands at 950, 880, and 800 cm^{-1}. In contrast, the spectrum of $[W_9ReO_{32}]^{5-}$ (both guanidinium and cesium salts) shows a pronounced splitting of the 800 cm^{-1} band (shoulders at 750 and 700 cm^{-1}) and an additional broad band of medium intensity at 570 cm^{-1}; see Figure 3. The same IR spectrum was observed for a solution of the anion extracted into benzene (see Experimental Section) and kept under nitrogen. Upon exposure of this solution to air, the IR spectrum slowly transformed (Figure 4) as oxidation to $[W_9Re^{VI}O_{32}]^{4-}$ took place.

The tetra-*n*-butylammonium salts of $[W_9Re^{VI}O_{32}]^{4-}$ and $[W_{10}O_{32}]^{4-}$ are isomorphous by X-ray powder diffraction. The ESR spectrum of the tungstorhenate was recorded on a frozen acetonitrile solution (77 K, 9.5 GHz) and on a polycrystalline 8% solid solution in $[(C_4H_9)_4N]_4[W_{10}O_{32}]$ (100 K, 35 GHz). The latter, Q-band, spectrum is shown in Figure 5, together with a simulation. The spectra indicate that the rhenium atom occupies a site of rhombic symmetry, and simulations were based on the spin Hamiltonian

$$H = g_x H S_x + g_y H S_y + g_z H S_z + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z$$

The ESR parameters obtained are given in Table 3.

The pronounced rhombic symmetry of the Re atom that is indicated by the ESR spectrum settles the question of that atom's location in the decatungstate framework, i.e. site I (Figure 1). The alternative position (II) would confer C_{4v} symmetry and a

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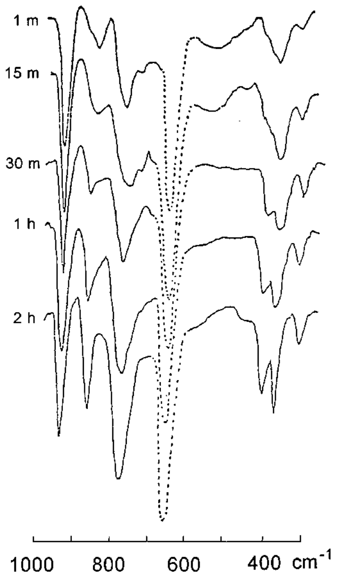

Figure 4. IR spectra of a benzene solution of $[W_9Re^{V}O_{32}]^{5-}$ that is undergoing aerial oxidation to $[W_9Re^{VI}O_{32}]^{4-}$. The broken line is a solvent absorption.

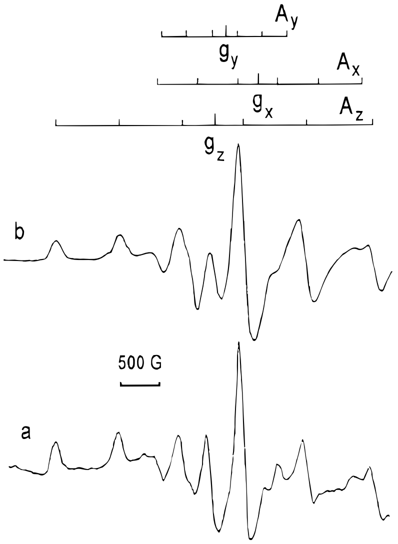

Figure 5. (a) Q-band (35 GHz) ESR spectrum of a polycrystalline 8% solution of $[W_9Re^{VI}O_{32}]^{4-}$ in $[(C_4H_9)_4N]_4[W_{10}O_{32}]$ at 100 K. (b) Simulation of (a) with the following parameters: g_x, 1.695; g_y, 1.665; g_z, 1.731; 10^4A_x, (−)252.6 cm^{-1}; 10^4A_y, (−)398.0 cm^{-1}; 10^4A_z, (−)653.3 cm^{-1}. Lorentzian line widths: *x*, 50 G; y, 70 G; z, 40 G.

Table 3. ESR Parameters for $[W_9Re^{VI}O_{32}]^{4-}$

g_x	1.69(1)	A_x[a]	(−)252(10)
g_y	1.66(1)	A_y	(−)398(10
g_z	1.730(2)	A_z	(−)653(5)

[a] ^{185,187}Re, $I = {}^5/_2$; units cm^{-1} × 10^{-4}.

simpler axial ESR spectrum. Furthermore, the location of Re in $[W_9ReO_{32}]^{n-}$ can account for the anomalous IR spectrum of the Re^{V} derivative as follows. The equatorial region of the tungstorhenate structure consists of one −W−O$_f$−Re− and three −W−O$_f$−W− groups; see Figure 1. The linear W−O$_f$−W(Re) bridges involve pπ → dπ overlap between oxygen p and tungsten/rhenium "d$_{xy}$" orbitals.[10] The reduction Re^{VII} → Re^{VI} → Re^{V} corresponds to $(d_{xy})^0 \rightarrow (d_{xy})^1 \rightarrow (d_{xy})^2$. In $[W_9Re^{V}O_{32}]^{4-}$, therefore, the rhenium's acceptor orbital is fully occupied, π-bonding from O$_f$ to Re is blocked, and the overall symmetry of the polyanion structure is reduced from that of the Re^{VI} and Re^{VII} derivatives.

Table 4. Electronic Absorption Maxima for $[W_9ReO_{32}]^{n-}$

anion	maxima cm^{-1} (absorbance (M^{-1} cm^{-1}))
$[W_9ReO_{32}]^{5-}$	13 000 (sh[a]), 18 300 (5850), 33 200 (10 000)
$[W_9ReO_{32}]^{4-}$	14 200 (sh), 19 700 (1160), 26 100 (4500), 33 400 (11 500), 38 000 (21 100)
$[W_9ReO_{32}]^{3-}$	33 500 (12 500), 38 100 (241 000)

[a] Shoulder.

The electronic absorption spectra of the three tungstorhenates are summarized in Table 4. In addition to the O → W charge transfer bands at >30 000 cm^{-1} (also observed for $[W_{10}O_{32}]^{4-}$), the Re^{VI} and Re^{V} derivatives exhibited intense bands in the visible and near-IR regions. For $[W_9Re^{VI}O_{32}]^{4-}$, the band at 26 000 cm^{-1} is assigned to an intervalence charge transfer (IVCT) transition, Re^{VI} → W^{VI}. The band occurs ca. 12 700 cm^{-1} higher in energy than the IVCT band of $[W_9W^{V}O_{32}]$,$^{5-}$[11] and this is consistent with the optical electronegativity[12] difference between Re and W that we had observed in the Keggin derivatives.[3] The bands at 19 700 and 14 200 cm^{-1} are assigned to d−d transitions[13] with intensities enhanced by the intervalence transition.[14] The spectrum of $[W_9Re^{V}O_{32}]^{5-}$ is dominated by the intense symmetrical band at 18 300 cm^{-1}. While this may be attributed to Re^{V} → W^{VI} IVCT, a similarly intense band (16 000 cm^{-1}, $\epsilon \sim$ 16 000 M^{-1} cm^{-1}) in the spectrum of $[W_8W_2{}^{V}O_{32}]^{6-}$ [11] might imply that the ground state of the tungstorhenate contains a contribution from the mixed-valence canonical form $[W_8W^{V}Re^{VI}O_{32}]^{5-}$.

Conclusions. Modest yields of the first example of a binary tungstorhenate poloxometalate are obtained by reaction of Re^{V} complexes with sodium tungstate. The new complex and its Re^{VI} and Re^{VII} isomorphs are the only known structural analogues of the D_{4h} "decatungstate" anion. The photochemical and catalytic activities of the latter species[15] suggest possible applications for the new tungstorhenates.

Acknowledgment. Support by the National Science Foundation is gratefully acknowledged. We thank Dr. Thomas A. Kennedy of the Naval Research Laboratory for recording the Q-band ESR spectrum.

Supporting Information Available: Listings of crystal data and structure refinement details, positional and thermal parameters, bond distances and angles, and interatomic distances (4 pages). Ordering information is given on any current masthead page.

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(10) The terminal M=O bond is presumed to define the local *z* axis for Re and W atoms.

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