Ti–O distance (Table IV) can be interpreted as symptomatic of a (delocalized) tendency for four-electron donation (i.e., using both ether lone pairs), taking $TiCl_2(THF)_4^+$ from the extreme of 13 toward 17 valence electrons. We shall expand on this idea in a subsequent description of a vanadium analogue of $[TiCl_2(THF)_4][ZnCl_3(THF)]$.

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Polyoxotungstate Anions Containing High-Valent Rhenium. 1. Keggin Anion Derivatives[1]

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The heteropolytungstate anions α-$PW_{11}ReO_{40}^{2-/3-/4-}$, α-$SiW_{11}ReO_{40}^{3-/4-/5-}$, $BW_{11}ReO_{40}^{4-/5-}$, and $SiW_{10}Re_2O_{40}^{2-/3-/4-}$ have been synthesized and isolated in the form of $(C_4H_9)_4N^+$ salts. The anions contain rhenium in oxidation states VII, VI, and V. X-ray powder diffraction establishes the monorhenate derivatives to have the Keggin heteropolyanion α-structure and the dirhenate, which was synthesized from β-A-$SiW_9O_{34}^{10-}$, probably to have the Keggin β-structure. Cyclic voltammograms of the monorhenates in CH_3CN show reversible redox processes coupling VII, VI, V, and IV oxidation states of rhenium. Electronic and, for Re(VI) anions, ESR spectra are reported. ESR parameters derived from simulated Q-band spectra are as follows: for $PW_{11}ReO_{40}^{3-}$, $g = 1.69$, 1.73, 1.792 and $a = 585$, 324, 838 G; for $SiW_{11}ReO_{40}^{4-}$, $g = 1.67$, 1.69, 1.788 and $a = 536$, 291, 776 G. The $(CH_3)_4N^+$ salt of $SiW_{11}ReO_{40}^{5-}$ shows electrochemically reversible oxidations to $SiW_{11}ReO_{40}^{4-}$ ($E_{1/2} = +0.28$ V vs. Ag/AgCl) and $SiW_{11}ReO_{40}^{3-}$ (+0.78 V) as well as pH-dependent reductions to $SiW_{11}Re^{IV}(OH)O_{39}^{5-}$ and $SiW_{11}Re^{III}(OH_2)O_{39}^{5-}$. Cyclic voltammograms of the dirhenate anions in CH_3CN show reversible redox processes coupling $SiW_{10}Re^{VII}_2O_{40}^{2-}$, $SiW_{10}Re^{VI}Re^{VI}O_{40}^{3-}$, $SiW_{10}Re^{VI}_2O_{40}^{4-}$, $SiW_{10}Re^{VI}Re^VO_{40}^{5-}$, and either $SiW_{10}Re^V_2O_{40}^{6-}$ or $SiW^{VI}_9W^VRe^{VI}Re^VO_{40}^{6-}$. The electronic spectra of $Re^{VII}Re^{VI}$- and $Re^{VI}Re^V$-containing anions have bands assigned as intervalence charge transfer at 8300 and 8500 cm^{-1}, respectively. The X-band ESR spectrum of the $Re^{VII}Re^{VI}$ anion shows it to be a trapped-valence species at 77 K. The other dirhenate anions are ESR silent.

Heteropoly- and isopolyanions of the transition elements of groups 5 and 6 constitute a large class of complexes[2] that attract current interest because of their perceived analogies to metal oxide lattices and their potential and realized catalytic applications.[3] Baker et al. recently discussed the characteristics of heteropolyanion-forming elements, notably their ionic radii (tetrahedral and octahedral coordination by oxide) and high positive charges.[4] Post transition elements like Te^{6+} and I^{7+} have appropriate sizes and charges and may indeed form polyanion-like structures such as $Co_4I_3O_{24}H_{12}^{3-}$ but these atoms lack the ability to form the short terminal M=O bonds that seem to be responsible for many of the redox and acid–base properties of "conventional" heteropolyanions.[1a,b] Among the other transition elements, rhenium appears to be well suited for polyoxoanions: Re_2O_7 is a polymer with equal numbers of ReO_4 tetrahedra and ReO_6 octahedra; the oxide hydration product $O_3ReOReO_3(H_2O)_2$ is a molecular species with corner-shared octahedral and tetrahedral rhenium atoms;[5] short terminal Re=O bonds are observed in complexes of Re(VII),

-(VI), and -(V) (e.g. $ReOF_5$, $ReOCl_4$, $ReOCl_5^{2-}$). Further, since ReO_3 and WO_3 are similar structurally, it would seem probable that one could prepare polytungstate anions in which one or more W(VI) atoms were replaced by Re(VI). Oxidation of these complexes could then lead to polyanions of uniquely low, perhaps zero, charge.

We report here the synthesis and properties of some rhenium-substituted polytungstates with the Keggin structure. Some years ago we described the ESR spectrum of α-$PW_{11}Re^{VI}O_{40}^{4-}$,[6] and Charreton and Meunier briefly reported the products of the reaction of $ReCl_6^{2-}$ and α-$SiW_{11}O_{39}^{8-}$ and α_2-$P_2W_{17}O_{61}^{10-}$.[7] The only other work with rhenium and polyanions appears to be solution studies of Re(V) with molybdate and molybdosilicate, from which the formation of several molybdorhenates was inferred.[8]

Experimental Section

Syntheses. The following salts were prepared according to published methods and were identified by infrared spectroscopy and, in the case of the heteropolyanions, by polarography: α-$[(n$-$C_4H_9)_4N]_4H_3PW_{11}O_{39}$;[9] $[(n$-$C_4H_9)_4N]ReOBr_4$;[10] α-$K_8SiW_{11}O_{39}$·$12H_2O$;[11] $[ReO_2(py)_4]Br$·$2H_2O$;[12] $K_9BW_{11}O_{39}$·xH_2O;[13] β-$Na_9HSiW_9O_{34}$·$23H_2O$.[14]

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Tetrabutylammonium α-11-Tungstorheno(V)phosphate (PW$_{11}$Re^{V}).
Addition of 0.92 g (1.2 mmol) of [(C$_4$H$_9$)$_4$N]ReOBr$_4$ to a stirred
solution of 3.2 g (1.0 mmol) of [(C$_4$H$_9$)$_4$N]$_4$H$_3$PW$_{11}$O$_{39}$ in 80 mL
of CH$_3$CN resulted in an immediate color change to purple. The
solution was filtered and allowed to crystallize for some hours. The
purple crystals formed were filtered off and washed with methanol.
Cyclic voltammetry (see below) indicated contamination with
[(C$_4$H$_9$)$_4$N]$_3$PW$_{12}$O$_{40}$, but this could be removed by recrystallization
from CH$_3$CN. Anal. Calcd for [(C$_4$H$_9$)$_4$N]$_4$PW$_{11}$ReO$_{40}$: C, 19.96;
H, 3.74; N, 1.45; P, 0.85; Re, 4.84; W, 52.27. Found: C, 20.16; H,
3.82; N, 1.38; P, 0.88; Re, 4.80; W, 52.42.

**Tetrabutylammonium α-11-Tungstorheno(VI)phosphate (PW$_{11}$-
Re^{VI}).** A dilute solution of bromine in CH$_3$CN was added dropwise
to a stirred solution of 0.5 g of the tetrabutylammonium salt of
PW$_{11}$Re^{V} until the color changed from red-purple to green. Dark
green crystals separated from the solution and were washed with
methanol. The product was isomorphous by X-ray powder diffraction
to α-[(C$_4$H$_9$)$_4$N]$_3$PW$_{12}$O$_{40}$, and its IR spectrum and cyclic voltam-
mogram were identical with those of the PW$_{11}$Re^{V} salt (with which
it is *not* isomorphous[15]).

Tetramethylammonium α-11-Tungstorheno(V)silicate (SiW$_{11}$Re^{V}).
A solution of 1.5 g (2.4 mmol) of [ReO$_2$(py)$_4$]Br·2H$_2$O in 50 mL of
water was added to a solution of 6.4 g (2 mmol) of α-
K$_8$SiW$_{11}$O$_{39}$·12H$_2$O in 100 mL of sodium acetate buffer, pH 5.5. The
mixture was stirred at 80–90 °C until the color changed from brown
through green to purple. After a further 10 min at 80 °C the solution
was allowed to cool and filtered to remove traces of insoluble matter.
Addition of 4 g of (CH$_3$)$_4$NBr yielded a dark precipitate that was
filtered off and recrystallized from warm water; yield ca. 6 g of dark
purple crystals. Anal. Calcd for [(CH$_3$)$_4$N]$_5$SiW$_{11}$ReO$_{40}$·4H$_2$O: C,
7.23; H, 2.05; N, 2.11; Si, 0.84; W, 60.95; Re, 5.61; H$_2$O, 2.17. Found:
C, 7.29; H, 2.11; N, 2.19; Si, 0.92; W, 60.37; Re, 5.72; H$_2$O, 2.27.

Tetrabutylammonium α-11-Tungstorheno(VI)silicate (SiW$_{11}$Re^{VI}).
A solution of 1 g of (n-C$_4$H$_9$)$_4$NBr in 10 mL of water was added to
a solution of 2 g of [(CH$_3$)$_4$N]$_5$SiW$_{11}$ReO$_{40}$·4H$_2$O in 50 mL of warm
water to give an immediate purple precipitate that was coagulated
by heating the mixture to boiling. The precipitate was filtered off,
washed with water, air-dried, and recrystallized from CH$_3$CN. In
this solvent the color of the solution slowly changed from red-purple
to green. Green crystals were obtained, which were filtered off and
washed with methanol. Anal. Calcd for [(C$_4$H$_9$)$_4$N]$_4$SiW$_{11}$ReO$_{40}$:
C, 19.97; H, 3.74; N, 1.45; Si, 0.76; W, 52.31; Re, 4.86. Found: C,
20.42; H, 3.71; N, 1.51; Si, 1.02; W, 52.01; Re, 4.91. The crystals
were isomorphous by X-ray powder diffraction with α-
[(C$_4$H$_9$)$_4$N]$_4$SiW$_{12}$O$_{40}$.

Tetrabutylammonium α-11-Tungstorheno(VII)silicate (SiW$_{11}$Re^{VII}).
A solution of 0.5 g of the green SiW$_{11}$Re^{VI} salt in 25 mL of CH$_3$CN
was treated dropwise with a dilute solution of bromine in CH$_3$CN
until the color changed from green to yellow. After some hours yellow
crystals formed. These were filtered off and washed with methanol.
The product was isomorphous by X-ray powder diffraction with
α-[(C$_4$H$_9$)$_4$N]$_3$PW$_{12}$O$_{40}$, and its IR spectrum and cyclic voltammo-
gram were identical with those of the SiW$_{11}$Re^{VI} salt.

Tetrabutylammonium α-11-Tungstorheno(VII)borate (BW$_{11}$Re^{VII}).
A solution of 3 g of Na$_9$BW$_{11}$O$_{39}$·xH$_2$O in 100 mL of acetate buffer,
pH 6, was mixed with a solution of 1.3 g of [ReO$_2$(py)$_4$]Br·2H$_2$O in
50 mL of water, and the mixture was heated to 80–90 °C. When
the color change (brown to green to purple) was complete, the mixture
was kept at 80 °C for 10 min, allowed to cool, and was filtered. About
2 g of (C$_4$H$_9$)$_4$NBr was added to the filtrate, and the resulting purple
precipitate was filtered off, washed with water, and allowed to dry.
A solution of the product in CH$_3$CN slowly turned green and deposited
about 3.8 g of small green crystals, probably [(C$_4$H$_9$)$_4$N]$_4$HBW$_{11}$-
ReO$_{40}$. A solution of the green crystals in CH$_3$CN was treated with
Br$_2$ in CH$_3$CN until the color became yellow. After some hours yellow
crystals formed. These were filtered off and washed with methanol.
Anal. Calcd for [(C$_4$H$_9$)$_4$N]$_4$BW$_{11}$ReO$_{40}$: C, 20.06; H, 3.76; N, 1.46;
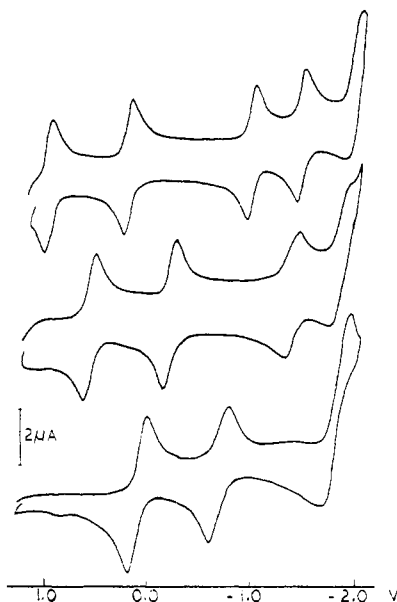
Figure 1. Cyclic voltammograms of 0.5 mM (Bu$_4$N)$_4$XW$_{11}$ReO$_{40}$
in CH$_3$CN (glassy-carbon electrode vs. Ag/AgCl; 0.1 M Bu$_4$NClO$_4$;
1.0 V min^{-1}): upper trace, X = P; middle trace, X = Si; lower trace,
X = B.

Table I. Cathodic Voltammetric Peak Potentials of
(Bu$_4$N)$_4$XW$_{11}$ReO$_{40}$ in Acetonitrile Solution[a]

X	E/V (ΔE^b/mV)			
	I (Re$^{7+/6+}$)	II (Re$^{6+/5+}$)	III (Re$^{5+/4+}$)	IV (?)
P	+0.90 (120)	+0.13 (110)	−1.07 (110)	−1.54 (90)
Si	+0.52 (120)	−0.25 (100)	−1.49 (110)	
B	+0.04 (110)	−0.76 (100)		

[a] Glassy-carbon electrode vs. Ag$^+$/AgCl; 0.50 mM in 0.10 M
Bu$_4$NClO$_4$; 1.00 V min^{-1}. [b] Separation of anodic and cathodic
peaks.

W, 52.53; Re, 4.87. Found: C, 20.17; H, 3.86; N, 1.45; W, 52.05;
Re, 4.91. The product was isomorphous by X-ray powder diffraction
with α-[(C$_4$H$_9$)$_4$N]$_4$SiW$_{12}$O$_{40}$.

**Tetrabutylammonium 10-Tungstodirheno(VI,VI)silicate (SiW$_{10}$-
Re^{VI}$_2$).** A mixture of 2.9 g (1 mmol) of β-Na$_9$HSiW$_9$O$_{34}$·23H$_2$O and
2 g (3.2 mmol) of [ReO$_2$(py)$_4$]Br·2H$_2$O in 80 mL of 1 M sodium
acetate–acetic acid, pH 6, was heated to boiling for 10 min during
which time the tungstosilicate dissolved and a deep violet color de-
veloped. Addition of a solution of 1 g of (C$_4$H$_9$)$_4$NBr in 20 mL of
water yielded a bulky dark precipitate that was filtered off, washed
with water, and allowed to dry. A solution of the precipitate in CH$_3$CN
slowly changed color from violet to green, and a green solid was
deposited. The product was filtered off and recrystallized from 40
mL of 1:4 CH$_3$CN–CH$_3$OH; yield 1.3 g of green crystals. Anal. Calcd
for [(C$_4$H$_9$)$_4$N]$_4$SiW$_{10}$Re$_2$O$_{40}$: C, 19.86; H, 3.46; N, 1.37; Si, 0.77;
W, 48.11; Re, 9.86. Found: C, 19.96; H, 3.74; N, 1.45; Si, 0.73; W,
47.8; Re, 9.68.

Physical Measurements. Cyclic voltammetry, dc polarography,
and controlled-potential coulometry were carried out as described
previously.[16] All potentials are reported relative to aqueous Ag$^+$/AgCl.
ESR spectra were recorded on JEOL MES-3X (X-band) and Varian
E-109Q (Q-band) spectrometers. Computer simulation of spectra
was made with CURHPER (J. H. Venables and A. S. Brill, University
of Virginia). Powder diffractograms were obtained with a Picker
powder diffractometer using Cu Kα radiation.

Results and Discussion

Monorhenium Derivatives, XW$_{11}$ReO$_{40}$$^{n-}$. Cyclic voltam-
mograms (Figure 1) of tetrabutylammonium salts of PW$_{11}$Re^{V},
SiW$_{11}$Re^{VI}, and BW$_{11}$Re^{VII} in CH$_3$CN show several reversible
redox processes, each of which was shown by controlled-po-
tential coulometry to involve one electron. Oxidized and re-

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salts of 3− and 4− Keggin α-anions are easily distinguished. Salts of
the 3− anions crystallize as needles, and salts of the 4− anions as poly-
hedral blocks. Values of d/n and relative intensities of the five strongest
lines in the powder diffractograms are as follows: for α-
[(C$_4$H$_9$)$_4$N]$_3$XM$_{12}$O$_{40}$, 4.55 (80), 4.44 (80), 3.69 (100), 2.97 (70), 2.78
(75); for α-[(C$_4$H$_9$)$_4$N]$_4$XM$_{12}$O$_{40}$, 4.67 (65), 4.17 (55), 3.77 (55), 3.62
(50), 2.97 (100).

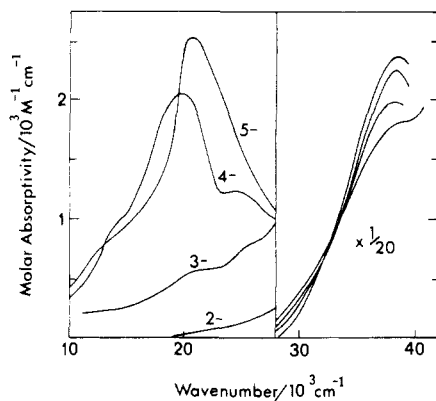(16) Prados, R. A.; Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2547.

Figure 2. Electronic absorption spectra of $PW_{11}ReO_{40}^{2-/3-/4-/5-}$ anions as Bu_4N^+ salts in CH_3CN.

duced derivatives of the heteropolyanions were prepared by chemical oxidation (see above) or controlled-potential electrolysis at a graphite-cloth electrode. For each of the three series of polyanions, the Re(VII) derivative is yellow, the Re(VI) derivative is dark green, and the Re(V) derivative is red-purple. The peak potentials, given in Table I, are strongly dependent upon anion charge as we have noted before.[17] In aqueous media the reduction potential of a Keggin anion decreases by ca. 160 mV as the charge increases by 1 unit. This trend has been rationalized on a simple electrostatic model that compares the reduction of a heteropolyanion to the electrostatic charging of a sphere.[17a] The greater variation of reduction potential observed in the present work (430 mV/unit charge) can readily by accounted for by the smaller dielectric constant of 0.1 M $(C_4H_9)_4NClO_4$ in CH_3CN compared with that of aqueous Na_2SO_4.

The third reduction waves observed in the cyclic voltammograms of $PW_{11}Re$ and $SiW_{11}Re$ are assigned to the reduction of Re(V) to Re(IV). Controlled-potential electrolysis of the phosphorus-centered anion at -1.24 V yielded a brown solution with an absorption spectrum similar to that produced in the aqueous reduction of $SiW_{11}Re^V$ (see below). The fourth reduction of $PW_{11}Re$ at -1.54 V probably corresponds to Re(IV) → Re(III), but this could not be confirmed readily. The Re(IV) derivatives and $BW_{11}Re^V$ were rapidly air oxidized in acetonitrile solutions, and SiW_1Re^V was slowly oxidized under the same conditions.

Hydrolytic stability of the heteropolyanions seems to be controlled by the overall anion charge, as has been observed for the unsubstituted Keggin anions. Thus, solutions of $PW_{11}Re^{VII}O_{40}^{2-}$ in moist CH_3CN are completely decolorized in about 45 min, whereas $SiW_{11}Re^{VII}O_{40}^{3-}$ and $BW_{11}Re^{VII}O_{40}^{4-}$ are indefinitely stable under similar conditions.

The IR spectra of the Re^V-, Re^{VI}-, and Re^{VII}-substituted anions are essentially indistinguishable from those of the corresponding $XW_{12}O_{40}^{n-}$ species. The electronic absorption spectra of $PW_{11}ReO_{40}^{n-}$ anions in acetonitrile solution are shown in Figure 2; band positions and extinction coefficients for all of the anions are summarized in Table II. All of the complexes show oxygen-to-tungsten charge transfer at ca. 38 000 cm^{-1}; the remaining bands are assigned tentatively to intensity-enhanced[18] d–d transitions and to heteronuclear (Re → W) intervalence charge transfer (IVCT). Analogous assignments have been made for V^{IV}-, Mo^V-, and W^V-substituted Keggin anions.[19] For the Re(VI) species the band at ca.

Table II. Electronic Spectral Data for $XW_{11}ReO_{40}^{n-}$ Anions in Acetonitrile Solution

X	band posn/cm^{-1} (ϵ/M^{-1} cm^{-1})
	Re^{VII} Anions
P	38 000 (48 000)
Si	38 200 (45 000)
B	39 000 (47 000)
	Re^{VI} Anions
P	21 000 (470), 25 300 (700),[a] 38 100 (46 000)
Si	19 600 (680), 25 200 (1040),[a] 38 000 (43 500)
B	20 900 (600), 25 900 (800),[a] 38 900 (47 000)
	Re^{V} Anions
P	14 000 (900),[a] 19 600 (2200), 25 400 (1400),[a] 37 900 (40 000)
Si	14 000 (950),[a] 19 800 (1940), 25 600 (1400),[a] 38 400 (41 200)
B	14 100 (800),[a] 20 400 (1540), 25 700 (1510),[a] 38 800 (41 200)
	Re^{IV} Anion
P	13 000 (800),[a] 20 800 (2600), 38 000 (38 000)

[a] Shoulder.

20 000 cm^{-1} is assigned to the $^2B_2 \rightarrow {}^2B_1$ transition (cf. 17 000–17 500 cm^{-1} for $ReOCl_5^-$ and $ReOCl_4^{20}$) and the band at ca. 25 000 cm^{-1} to IVCT. In C_{4v} symmetry a lower energy d–d band ($^2B_2 \rightarrow {}^2E$) should be observed (12 000–12 800 cm^{-1} for $ReOCl_5^-$); none could be resolved for the heteropolyanions. A rough calculation, based on the anisotropy of the ESR g values (see below), suggests that the ^2E level is split by approximately 1300 cm^{-1} and this may account for the lack of resolvable intensity on the low-energy side of the 20 000-cm^{-1} band.

Assignments for the Re(V) and Re(IV) anions are even less certain. In the spectrum of $ReOCl_5^{2-}$, four d–d bands between 9000 and 24 000 cm^{-1} were assigned to $^1A_1(b_2^2) \rightarrow {}^1E(b_2e)$, $^1A_2(b_1b_2)$ and the corresponding triplet transitions.[21] The heteropolyanion bands at 14 000 and 20 000 cm^{-1} may therefore correspond to $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_2$, and the band at 25 000 cm^{-1}, to IVCT. The spectrum of $Re(OH)Br_5^{2-}$ shows numerous weak bands between 5500 and 15 150 cm^{-1} that were assigned to d–d transitions in C_{4v} symmetry.[22] The shoulder at 13 000 cm^{-1} in the spectrum of the Re(IV) heteropolyanion may correspond to one of the d–d bands and the more intense band at 20 800 cm^{-1} to IVCT.

The X-band ESR spectrum of $(Bu_4N)_4PW_{11}ReO_{40}$ was reported some years ago.[6] Owing to the large hyperfine coupling parameters and consequent Breit–Rabi effects, a wholly satisfactory analysis of the spectrum was not possible. We have therefore recorded spectra of $PW_{11}Re$ and $SiW_{11}Re$ anions as polycrystalline solid solutions in $(Bu_4N)_3PW_{12}O_{40}$ and $(Bu_4N)_4SiW_{12}O_{40}$ at 35 GHz (Q band). Experimental and simulated spectra are shown in Figures 3 and 4 together with the experimental X-band spectra. Derived parameters based on the conventional spin Hamiltonian for a d^1 ion in a rhombic field

$$\mathcal{H} = \beta[g_xH_xS_x + g_yH_yS_y + g_zH_zS_z] + A_xS_xI_x + A_yS_yI_y + A_zS_zI_z$$

are given in Table III. The ESR spectra, both at X and Q band, could not be observed at temperatures above 150–200 K, and so no direct measure of isotropic g and a was possible.

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(18) Enhancement of d–d band intensities by 2–3 orders of magnitude in mixed-valence complexes is not uncommon. Particularly unambiguous examples are seen in some vanadium(IV,V) species: Babonneau, F.; Sanchez, C.; Livage, J.; Launay, J. P.; Daoudi, M.; Jeannin, Y. *Nouv. J. Chim.* **1982**, *6*, 353.

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Table III. ESR Spin Hamiltonian Parameters of $XW_{11}Re^{VI}$ Anions at ca. 100 K[a]

anion	g_x	g_y	g_z	A_x/cm^{-1}	A_y/cm^{-1}	A_z/cm^{-1}
$PW_{11}ReO_{40}{}^{3-}$	1.69 (1)[b]	1.73 (1)	1.792 (2)	0.0462 (10)[b,c]	0.0262 (10)	0.0701 (5)
$SiW_{11}ReO_{40}{}^{4-}$	1.67 (1)	1.69 (1)	1.788 (2)	0.0418 (10)	0.0231 (10)	0.0639 (5)

[a] Owing to unfavorable relaxation times, no spectra could be observed at temperatures above ca. 150 K. [b] Estimated uncertainty in last digit(s). [c] Values of A_i (in gauss) are 585, 324, 838, and 536, 291, 776, respectively.

Figure 3. (a) X-Band ESR spectrum of $(Bu_4N)_3PW_{11}ReO_{40}$ in CH_3CN at 77 K. (b) Observed (lower) and simulated (upper) Q-band ESR spectra of $(Bu_4N)_3PW_{11}ReO_{40}$ as a (polycrystalline) 8% solid solution in $(Bu_4N)_3PW_{12}O_{40}$ at 100 K.

Figure 4. (a) X-band ESR spectrum of $(Bu_4N)_4SiW_{11}ReO_{40}$ in CH_3CN at 77 K. (b) Observed (lower) and simulated (upper) Q-band ESR spectra of $(Bu_4N)_4SiW_{11}ReO_{40}$ as a (polycrystalline) 10% solid solution in $(Bu_4N)_4SiW_{12}O_{40}$ at 100 K.

The orthorhombic site symmetry observed for Re^{6+} in the Keggin structure is not unexpected of course; an individual metal atom in this structure has maximum point symmetry of C_s, and rhombic ESR spectra are observed for W^{5+}, Mo^{5+},

Table IV. Cathodic Voltammetric Peak Potentials of $SiW_{11}ReO_{40}{}^{5-}$ in Aqueous Solution[a]

pH	Re redn[b]	W redn[b]
1.0	+0.75, +0.25, −0.45[c]	−0.57, −0.71
2.0	+0.75, +0.24, −0.53[c]	−0.65, −0.78
3.0	+0.75, +0.24, −0.60[c]	−0.73, −0.84
3.2	+0.75, +0.25, −0.60, −0.62[d]	−0.75, −0.88
3.4	+0.76, +0.24, −0.60, −0.65[d]	−0.77, −0.89
4.0	+0.74, +0.25, −0.62, −0.69[d]	−0.80, −0.95
5.0	e, +0.24, −0.63, −0.78[d]	−0.88, −0.98
6.0	e, +0.24, −0.64, −0.84[d]	−0.94, f

[a] 1.0 M Na_2SO_4 with bisulfate, monochloracetate, or acetate buffers; glassy-carbon electrode vs. Ag/AgCl; 1.0 V min^{-1}. [b] Except where noted each wave corresponded to one electron and had $E_{pa} - E_{pc} \approx 60$ mV. [c] Two-electron reduction, $E_{pa} - E_{pc} \approx$ 240–280 mV. [d] Irreversible, two-electron oxidation peak at −0.35 to −0.46 V. [e] Not observed owing to rapid hydrolysis; anodic peak at +0.81 V. [f] Not observed.
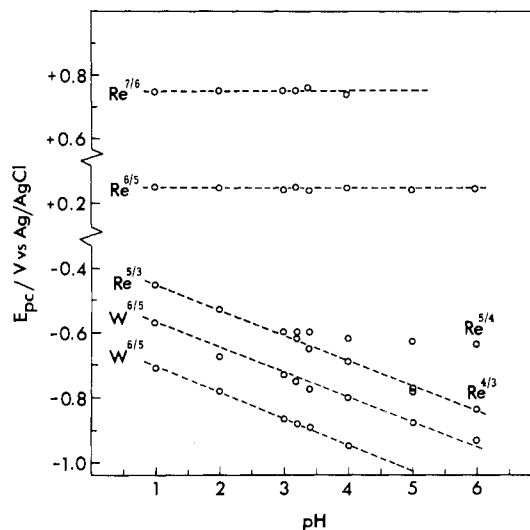

Figure 5. Variation of cathodic peak potentials in cyclic voltammograms of $[(CH_3)_4N]_5SiW_{11}ReO_{40}$ recorded at different pH.

and $RuNO^{2+}$ in Keggin polytungstates.[23]

The tetramethylammonium salt of $SiW_{11}Re^VO_{40}{}^{5-}$ is water soluble, and a more extensive electrochemical study of the anion was made. Polarograms and cyclic voltammograms were recorded on freshly prepared solutions in the range 1 < pH < 6; the results are summarized in Table IV and Figure 5. In Figure 6, which shows a cyclic voltammogram recorded at pH 5.0, reversible oxidation of $SiW_{11}Re^V \rightarrow SiW_{11}Re^{VI} \rightarrow SiW_{11}Re^{VII}$ is observable at +0.25 and +0.75 V, respectively, although the oxidized anions are quite rapidly hydrolyzed at this pH.[24] The four reductions at negative potentials each involve one electron (confirmed by controlled-potential electrolysis) and for reasons discussed below are attributed to $Re^{5+/4+}$, $Re^{4+/3+}$, and two $W^{6+/5+}$ reductions. Note that the last two processes are reversible ($\Delta E_{pp} \sim 60$ mV) whereas the first two are irreversible with a single two-electron-oxidation

(23) (a) Prados, R. A.; Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2547. (b) Wendel, C. H.; Pope, M. T., unpublished results.
(24) When the sweep rate was increased to 400 V min^{-1}, the cathodic and anodic peak heights for the $Re^{5+/6+}$ and $Re^{6+/7+}$ processes became equal to those of the one-electron reductions at negative potentials.
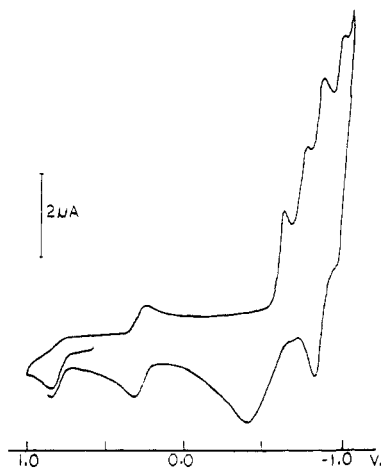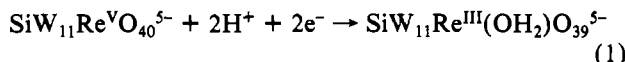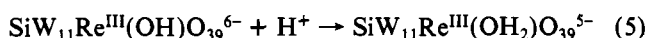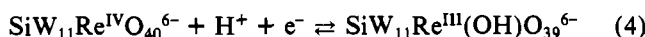
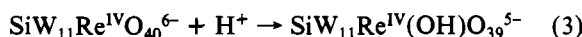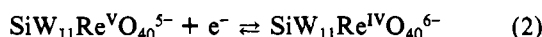**Figure 6.** Cyclic voltammogram of 0.5 mM $[(CH_3)_4N]_5SiW_{11}ReO_{40}$ at pH 5.0, sodium acetate buffer (glassy-carbon electrode vs. Ag/AgCl; 1.0 V min^{-1}).

peak. Voltammograms in which the voltage sweep is reversed immediately following the first reduction show the reduction to be reversible at pH 4 (sweep rate 1.0 V min^{-1}) but to be irreversible when a delay of 45 s is introduced at the cathodic switching potential. At pH 6 the reduction is reversible whether or not there is a delay. Analogous experiments conducted on the second reduction wave, the potential of which varies continuously with pH over the range studied, yield similar results at pH 4 and 6. At pH ≤3 both reductions have coalesced into an irreversible ($\Delta E_{pp} \sim 300$ mV) pH-dependent two-electron redox process. We interpret these results as follows. At pH ≤3.0

$$SiW_{11}Re^V O_{40}{}^{5-} + 2H^+ + 2e^- \rightarrow SiW_{11}Re^{III}(OH_2)O_{39}{}^{5-} \quad (1)$$

At pH >3.0

$$SiW_{11}Re^V O_{40}{}^{5-} + e^- \rightleftharpoons SiW_{11}Re^{IV}O_{40}{}^{6-} \quad (2)$$

$$SiW_{11}Re^{IV}O_{40}{}^{6-} + H^+ \rightarrow SiW_{11}Re^{IV}(OH)O_{39}{}^{5-} \quad (3)$$

$$SiW_{11}Re^{IV}O_{40}{}^{6-} + H^+ + e^- \rightleftharpoons SiW_{11}Re^{III}(OH)O_{39}{}^{6-} \quad (4)$$

$$SiW_{11}Re^{III}(OH)O_{39}{}^{6-} + H^+ \rightarrow SiW_{11}Re^{III}(OH_2)O_{39}{}^{5-} \quad (5)$$

In reaction 1 electrons are added to the antibonding (e) orbital of the terminal Re=O bond, thereby weakening it and rendering the oxygen susceptible to protonation. The pH dependence (60 mV/pH unit) of the reduction potential at 1 < pH < 3 demonstrates that two protons are involved in this reduction. At pH >3 one electron is reversibly added to the Re(V) anion (eq 2) in a pH-independent step. The resulting Re(IV) species is subsequently protonated at the terminal Re=O oxygen for the reasons cited above. This reaction (3) accounts for the irreversibility observed at pH 4 with slow sweep rates. Reactions 4 and 5 account similarly for the observed behavior of the second reduction. The whole reduction process, (1) or (2)–(4), converts a terminal oxo oxygen to a terminal water molecule. A similar net reaction has been reported for $SiW_{11}V^{IV}O_{40}{}^{6-}$ isomers, yielding $SiW_{11}V^{III}$-$(OH_2)O_{39}{}^{5-},[25]$ and probably has also occurred with the "brown" reduced polytungstates, which are believed to contain $W^{IV}.[26]$

Controlled-potential electrolysis of $SiW_{11}Re^V O_{40}{}^{5-}$ in an acetate buffer, pH 4.7, was carried out at −0.65, −0.80, and −0.95 V. In each case one electron per anion was added to yield violet, green, and dark blue solutions, respectively. The electronic absorption spectra of these solutions are shown in
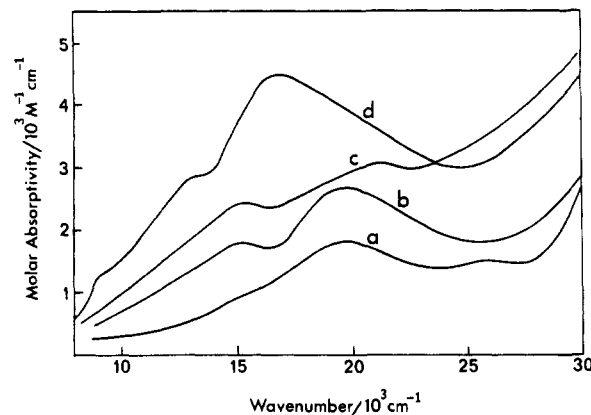

Figure 7. Electronic absorption spectra (aqueous acetate buffer, pH 4.7): (a) $SiW_{11}Re^V(O)O_{39}{}^{5-}$; (b) $SiW_{11}Re^{IV}(OH)O_{39}{}^{5-}$; (c) $SiW_{11}Re^{III}(OH_2)O_{39}{}^{5-}$; (d) $HSiW_{10}W^V Re^{III}(OH_2)O_{39}{}^{5-}$.
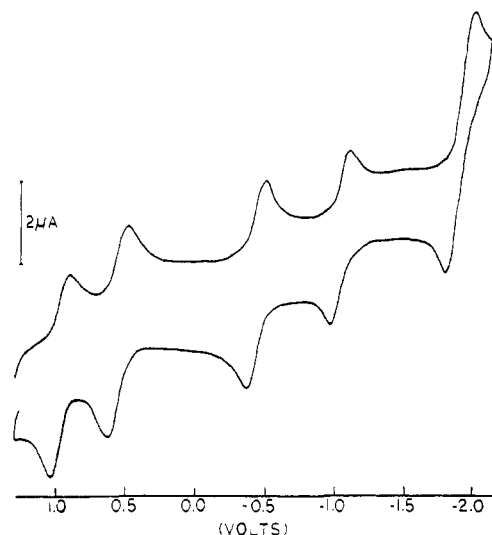
Figure 8. Cyclic voltammogram of 0.5 mM $(Bu_4N)_5SiW_{10}Re_2O_{40}$ in CH_3CN (glassy-carbon electrode vs. Ag/AgCl; 0.1 M Bu_4NClO_4; 1.0 V min^{-1}).

Figure 7. The band positions and intensities of the violet product, $SiW_{11}Re(OH)O_{39}{}^{5-}$, correspond well with those for the Re(IV) derivative generated in CH_3CN (Table II). The green and blue species are considered to be $SiW_{11}Re^{III}$-$(OH_2)O_{39}{}^{5-}$ and $HSiW_{10}W^V Re^{III}(OH_2)O_{39}{}^{5-}$, respectively. Note that only the second of these shows an absorption band at 8700 cm^{-1} characteristic of $W^V \rightarrow W^{VI}$ IVCT.[19]

The Dirhenium Derivative $SiW_{10}Re_2O_{40}{}^{4-}$. This material was isolated from a reaction between β-$SiW_9O_{34}{}^{10-}$ and $[ReO_2$-$(py)_4]^+$ (Experimental Section). Many unsuccessful attempts were made to produce a trirhenium derivative, by using a large excess of rhenium or by working at a higher pH (8–9) where $SiW_9O_{34}{}^{10-}$ is more stable. It is possible, and indeed likely, that some SiW_9Re_3 species was formed in these attempts, but only salts of $SiW_{10}Re_2O_{40}{}^{n-}$ occasionally mixed with $SiW_{11}ReO_{40}{}^{n-}$ could be isolated. From their colors, the salts precipitated from the aqueous reaction mixture contain Re(V). They spontaneously are oxidized to the Re(VI) derivatives upon crystallization from CH_3CN. The cyclic voltammogram of $(Bu_4N)_4SiW_{10}Re_2O_{40}$ shown in Figure 8 demonstrates the absence of any significant quantities of $SiW_{11}ReO_{40}{}^{4-}.[27]$ The four quasi-reversible (ΔE ca. 110 mV) one-electron-reduction steps at +0.91, +0.50, −0.48, and −1.09 V are assigned re-

(25) Hervé, G.; Tézé, A.; Leyrie, M. *J. Coord. Chem.* **1979**, *9*, 245.
(26) Jeannin, Y.; Launay, J. P.; Sedjadi, M. A. S. *Inorg. Chem.* **1980**, *19*, 2933.

(27) Other preparations yielded products with voltammograms that showed small waves with potentials close to those observed for α-$SiW_{11}ReO_{40}{}^{4-}$ (Table I). It is possible, however, in view of the starting material, that the impurity was one or more of the β-isomers of $SiW_{11}Re$.
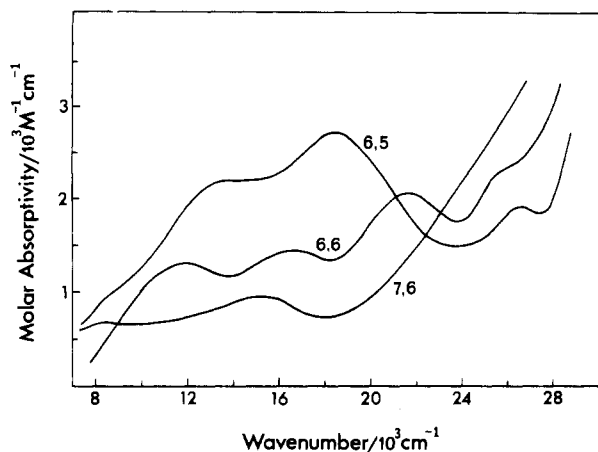
Figure 9. Electronic absorption spectra of $SiW_{10}Re_2O_{40}^{3-/4-/5-}$ anions as Bu_4N^+ salts in CH_3CN. Curves are labeled with oxidation states of Re.

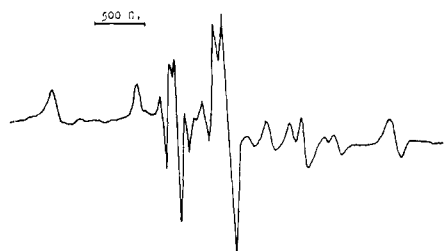**Figure 10.** X-Band ESR spectrum of $(Bu_4N)_3SiW_{10}Re^{VII}Re^{VI}O_{40}$ in CH_3CN at 77 K.

spectively to $Re_2^{7+,7+/7+,6+}$, $Re_2^{7+,6+/6+,6+}$, $Re_2^{6+,6+/6+,5+}$, and $Re_2^{6+,5+/5+,5+}$. The assignment of the fourth reduction cannot be made with complete confidence for upon controlled-potential electrolysis at -1.40 V the solution became blue ($?W^{5+}$) and the electrolysis resulted in irreversible decomposition of the anion. Other bulk electrolyses, oxidations at $+0.90$ and $+1.30$ V and reduction at -0.60 V, proceeded smoothly and quantitatively.

The fully oxidized yellow anion $SiW_{10}Re_2O_{40}^{2-}$ is slowly hydrolyzed in wet organic solvents and is best isolated by bromine oxidation of $(Bu_4N)_4SiW_{10}Re_2O_{40}$ in CH_3CN followed by rapid addition of ether to precipitate the salt. The latter is indefinitely stable as a dry solid. The electronic absorption spectra of the three reduced anions, $SiW_{10}Re^{VII}Re^{VI}$ (green), $SiW_{10}Re^{VI}_2$ (green) and $SiW_{10}Re^{VI}Re^V$ (violet), are illustrated in Figure 9 and summarized in Table IV. The most significant features of these spectra are the bands at 8300 and 8500 cm^{-1} for the mixed-valence anions. These are assigned to Re(VI) $\rightarrow$ Re(VII) and Re(V) $\rightarrow$ Re(VI) IVCT bands since they appear at similar energies to the analogous W(V) $\rightarrow$ W(VI), Mo(V) $\rightarrow$ Mo(VI), and V(IV) $\rightarrow$ V(V) bands in heteropolyanions.[19]

The X-band ESR spectrum of a frozen solution of $(Bu_4N)_3SiW_{10}Re^{VII}Re^{VI}O_{40}$ at 77 K is shown in Figure 10. The spectrum is similar to that of $SiW_{11}ReO_{40}^{4-}$ (Figure 4a) and demonstrates that the dirhenate anion is a class II mixed-valence species with valences trapped at 77 K. The Re^{VI}_2 and $Re^{VI}Re^V$ anions gave no ESR spectra at 77 K or above.

The questions arise as to whether the $SiW_{10}Re_2O_{40}$ anions have Keggin α- or β-framework and, further, which one(s) of the several possible positional isomers[28] have been formed. We are unable to provide incontrovertible answers to these questions with the presently available results, but we believe there is some evidence in favor of the formulation $1,2$-β-

$SiW_{10}Re_2O_{40}^{n-}$ with adjacent corner-shared ReO_6 octahedra.[29] First, the complexes were prepared from structurally characterized[30] β-$SiW_9O_{34}^{10-}$ (β-SiW_{12} with octahedra 1, 2, and 3 missing). Second, the X-ray powder diffractograms of α- and β-$(Bu_4N)_4SiW_{12}O_{40}$ are very different, and the diffractogram of $(Bu_4N)_4SiW_{10}Re_2O_{40}$ is similar (but not identical) to that of the β-isomer.[31] Solid solutions containing ca. 40% $SiW_{10}Re_2O_{40}^{4-}$ in β-$(Bu_4N)_4SiW_{12}O_{40}$ are readily obtained, and these solid solutions are isomorphous with the host crystals. Third, the observation of IVCT bands in the optical spectra of the mixed-valence anions indicates the presence of isomers with adjacent ReO_6 octahedra. Fourth, the absence of an observable triplet-state ESR spectrum for $SiW_{10}Re^{VI}_2O_{40}^{4-}$ suggests that there are no isomers with nonadjacent ReO_6 octahedra.[32] Fifth, the spectrum of $Cl_4ORe^{VI}ORe^{VI}OCl_4^{2-}$ shows two intensity-enhanced d–d bands at 12 200 and 16 000 cm^{-1};[33] these may be compared with the bands at 12 100 and 16 600 cm^{-1} in the spectrum of $SiW_{10}Re_2O_{40}^{4-}$.

None of the above arguments is sufficiently strong to characterize the structure unambiguously; such characterization would require good-quality,[34] rhenium-decoupled ^{183}W NMR spectroscopy of $SiW_{10}Re_2O_{40}^{2-}$ solutions. In view of the quantities of compound required for these measurements, its unfavorable solubility, and poor hydrolytic stability, NMR measurements were not seriously contemplated.

Conclusions. This work reemphasizes the importance of anion charge in controlling the hydrolytic stability of heteropolyanions. Although the substitution of rhenium for tungsten in the Keggin structure leads to anions of low charge, $PW_{11}ReO_{40}^{2-}$ and $SiW_{10}Re_2O_{40}^{2-}$, these species are readily hydrolyzed in aqueous media. On the other hand, other anions containing Re(VII), $SiW_{11}ReO_{40}^{3-}$ and $BW_{11}ReO_{40}^{4-}$, are stable and provide rare examples of $Re^{VII}O_6$ coordination. The redox chemistry of the new polyanions leads to a "rational" sequence of rhenium reduction potentials uncomplicated by disproportionation and allows us directly to compare the potentials of Re, W, Mo, and V.

(28) For α-$SiW_{10}Re_2O_{40}$, 5 isomers; for β-$SiW_{10}Re_2O_{40}$, 14 isomers. See: Reference 2a, p 27.

(29) The numbering of octahedra in β-$XZ_{12}O_{40}$ places the rotated W_3O_{13} group with positions 10, 11, and 12. See: Reference 2a, pp 142–6.
(30) Robert, F.; Tézé, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 11.
(31) The β-SiW_{12} salt is orthorhombic ($P2_12_12_1$, a = 29.277 Å, b = 22.181 Å, c = 15.381 Å): Fuchs, J.; Thiele, R.; Palm, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *86B*, 161. The $SiW_{10}Re_2$ salt is monoclinic ($P2_1/c$, a = 26.354 Å, b = 16.036 Å, c = 24.974 Å, β = 98.47°).
(32) Such triplet spectra, albeit for V(IV), have been observed in the isomer mix of α-$PW_{10}V^{IV}_2O_{40}^{7-}$: Pope, M. T.; O'Donnell, S. E.; Prados, R. A. *Adv. Chem. Ser.* **1976**, *No. 150*, 85. Single "adjacent" isomers of $PW_{10}Mo^V_2O_{40}^{5-}$ and $P_2W_{16}V^V_2O_{62}^{10-}$ are ESR silent.
(33) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054.
(34) It would be essential to observe W–W couplings and to establish connectivities by two-dimensional techniques. See: Domaille, P. J.; Knoth, W. H. *Inorg. Chem.* **1983**, *22*, 818.