

A Hydrolysis-Resistant Terminal ME Bond (M = Nb; E = S, Se; M = Ta; E = S) in a Chalcogenido-Substituted Mixed-Metal Polyoxoanion

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The hydrolysis of the terminal niobium or tantalum sulfido and selenido multiple bond has been little examined despite its many other interesting reactions, structures, and properties.^{1–7} Though studies have been rare, several compounds have been previously reported or assumed to be moisture sensitive.^{1d,2,3b,4b,6a,c} In this communication, we examine the hydrolytic stability of the terminal ME bond in a series of group 5 mixed-metal polytungstophosphates [PW₁₁O₃₉ME]^{4–} of the Keggin structure (Figure 1a),^{8,9} whose syntheses are also given. In marked contrast to [W₅O₁₈NbE]^{3–} (E = S,² Se) (Figure 1b) and related terminal sulfido and selenido complexes, we find that the ME bond (M = Nb, E = S, Se; M = Ta, E = S) in [PW₁₁O₃₉ME]^{4–} exhibits superior hydrolytic stability.¹⁰

Although isostructural mononuclear metal oxoanions and their chalcogenido homologs have been prepared and studied extensively,¹¹ analogous polyoxoanions⁸ are limited to one example, [W₅O₁₈ME]^{3–} (M = Nb, Ta, E = O, S) (Figure 1b).² Its synthesis takes advantage of a substitution labile {MO}³⁺ fragment incorporated into a substitution-inert polytungstate. Using this preparative strategy, attempts at oxo/chalcogenido

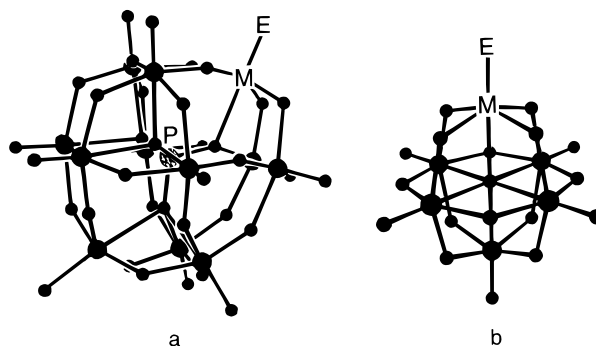
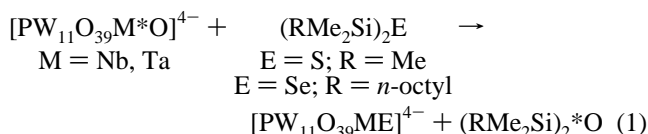


Figure 1. Structural representation of the monosubstituted mixed-metal (a) polytungstophosphate [PW₁₁O₃₉ME]^{4–} and (b) polytungstate [W₅O₁₈ME]^{3–} (M = Nb, Ta; E = O, S, Se). Solid spheres are tungsten (large) and oxygen (small) atoms.

ligand substitution reactions^{2,12} (eq 1) of [PMW₁₁O₄₀]^{4–} (M =



Nb, Ta)¹³ with excess bis(trialkylsilyl) chalcogenide¹⁴ yielded [PW₁₁O₃₉ME]^{4–} (E = S, Se).¹⁵ These compounds are observed as the sole product in high yield except for [PW₁₁O₃₉TaSe]^{4–}, whose yield was hampered by an additional product in the reaction mixture observed by ³¹P NMR. Oxygen atom transfer from [PMW₁₁O₄₀]^{4–} to (RMe₂Si)₂E (E = S, Se) was quantitative by ¹⁷O NMR spectroscopy.¹⁶

The IR spectra of [PW₁₁O₃₉MS]^{4–} (M = Nb, Ta) display the principal polyoxoanion bands of the oxo analogues¹³ with the exception of the disappearance of a band at 941 cm^{–1} and the appearance of a band at 484 cm^{–1} (M = Ta) and an overlapping band at 516 cm^{–1} (M = Nb). These bands are in excellent

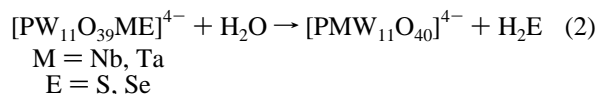
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- The tetra-*n*-butylammonium cation is the counterion of the polyoxoanions in this communication.
- In the polyoxoanion literature,^{8,22} the term *hydrolysis* refers usually to the *decomposition* of the polyoxoanion structure by loss of one or more of the metal centers that comprise the metal–oxygen framework. In this communication, hydrolysis is used to refer only to the reaction of water with the {ME}³⁺ fragment (E = O, S, Se) incorporated into the polyoxoanion and not to the supporting framework unless otherwise specified.
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- (RMe₂Si)₂E: (a) E = S; R = Me (Aldrich Chemical Co.). (b) E = Se, R = *n*-octyl; E = Te, R = *tert*-butyl (Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1354. Reference 12b).
- The preparation and analytical and characterization data for [PW₁₁O₃₉ME]^{4–} (M = Nb, Ta; E = S, Se) are given in the Supporting Information.
- Polyoxoanions were labeled with isotopically enriched H₂O (10% ¹⁷O), and ¹⁷O NMR chemical shifts were referenced externally vs H₂O. ¹⁷O NMR (40.7 MHz, dmf): δ[PW₁₁O₃₉M¹⁷O]^{4–} 831 (M = Nb), 687 (M = Ta) ppm; δ(RMe₂Si)₂O 41 (R = Me), 30 (R = *n*-octyl) ppm.

agreement with those reported earlier for the terminal MS stretch in $[\text{W}_5\text{O}_{18}\text{MS}]^{3-}$ at 481 (M = Ta) and 510 cm^{-1} (M = Nb).² No MSe stretch was detected by IR spectroscopy above 350 cm^{-1} in the selenido derivatives. Positive ion fast atom bombardment mass spectroscopic (FAB-MS) measurements of (*n*-Bu₄N)₄[PW₁₁O₃₉ME] (M = Nb, Ta; E = S, Se) exhibit peak envelopes for the corresponding protonated and tetra-*n*-butylammonium-substituted molecular and reduced ions.^{13,17}

Ligand substitution of the terminal niobium oxygen atom in $[\text{MPW}_{11}\text{O}_{40}]^{4-}$ (M = Nb, Ta) is also supported by multinuclear NMR spectroscopy. The appearance of six resonances in their ¹⁸³W NMR spectra is consistent with the C_{3v} symmetry shown in Figure 1 and is similar to the case of their oxo analogs.¹⁸ The ⁷⁷Se NMR spectra of $[\text{PW}_{11}\text{O}_{39}\text{MSe}]^{4-}$ show single resonances at 2019 (M = Nb) and 1304 (M = Ta) ppm in dmf. The chemical shift of $[\text{PW}_{11}\text{O}_{39}\text{NbSe}]^{4-}$ is downfield of $[\text{NbW}_5\text{O}_{18}\text{Se}]^{3-}$ (1795 ppm), which was prepared by a reaction similar to eq 1.¹⁹ Considering the wide range of ⁷⁷Se NMR chemical shifts displayed by metal selenides,^{12c} the chemical shift of $[\text{PW}_{11}\text{O}_{39}\text{TaSe}]^{4-}$ is similar to shifts reported for $[\text{TaSe}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}]$ (1518 ppm)^{1h} and Cp*Ta(Se)X (X = I, R, SeH, H) (range: 1990–2363 ppm).^{1j} The magnitude of the ³¹P NMR chemical shifts of the metal oxo species compared to the heavier chalcogenido congeners reflects the decrease in Pauling electronegativity down group 16.²⁰

We assessed the lability of the terminal oxygen atom of the $\{\text{NbO}\}^{3+}$ fragment in $[\text{PNbW}_{11}\text{O}_{40}]^{4-}$ with respect to oxygen atom exchange with H₂O by ¹⁷O NMR spectroscopy. When a 0.05 M solution of $[\text{PNbW}_{11}\text{O}_{40}]^{4-}$ in distilled dmf was mixed with 50 equiv of H₂O (10% ¹⁷O enriched), little detectable exchange occurred at either room temperature or 80 °C over several days. If CF₃SO₃H was added to this solution, however, exchange occurred readily. This observation is in contrast to the facile oxygen atom exchange of $\{\text{NbO}\}^{3+}$ in $[\text{NbW}_5\text{O}_{19}]^{3-}$ with H₂O.²¹ This difference in reactivity is also supported by the more forcing conditions required to accomplish the oxo/sulfido or oxo/selenido ligand substitution reactions for $[\text{PMW}_{11}\text{O}_{40}]^{4-}$ (M = Nb, Ta) than for $[\text{NbW}_5\text{O}_{19}]^{3-}$.

The decreased lability of the terminal NbO bond in the polytungstophosphate presaged the hydrolytic stability of the heavier chalcogenido bond in the sulfido and selenido derivatives (eq 2). Approximately 10% or less of 0.05 M dmf



solutions of $[\text{PW}_{11}\text{O}_{39}\text{ME}]^{4-}$ (M = Nb, E = S, Se; M = Ta, E = S) containing 50 equiv of H₂O converted to $[\text{PMW}_{11}\text{O}_{40}]^{4-}$ at room temperature over a 2 week period as determined by ³¹P NMR. The hydrolysis of $[\text{PW}_{11}\text{O}_{39}\text{TaSe}]^{4-}$ was appreciably faster. In comparison, the MS bond in $[\text{W}_5\text{O}_{18}\text{MS}]^{3-}$ hydrolyzes

completely to MO within several days with 5 equiv of H₂O in acetonitrile² and the NbSe bond in $[\text{W}_5\text{O}_{18}\text{NbSe}]^{3-}$ has a half-life of approximately 6 h in wet dmf as judged by IR spectroscopy.

The addition of CF₃SO₃H to a H₂O-treated dmf solution of $[\text{PW}_{11}\text{O}_{39}\text{NbS}]^{4-}$ did not accelerate its hydrolysis greatly but caused $[\text{PW}_{11}\text{O}_{39}\text{TaS}]^{4-}$ to hydrolyze rapidly under the same conditions. Likewise, a H₂O-treated dmf solution of $[\text{PW}_{11}\text{O}_{39}\text{NbSe}]^{4-}$ hydrolyzed only slightly when exposed to air, but this increased the rate of hydrolysis of $[\text{PW}_{11}\text{O}_{39}\text{TaSe}]^{4-}$. All the compounds, $[\text{PW}_{11}\text{O}_{39}\text{ME}]^{4-}$ (M = Nb, Ta; E = S, Se), formed $[\text{PMW}_{11}\text{O}_{40}]^{4-}$ when reacted with H₂O in the presence of a metal, e.g. AgNO₃, CuCl, or TiCl₃, that abstracted the chalcogen. No detectable H₂O exchange or hydrolytic decomposition of the supporting $\{\text{PW}_{11}\text{O}_{39}\}^{7-}$ polytungstate framework was observed during either exchange or hydrolysis experiments as monitored by ¹⁷O or ³¹P NMR spectroscopy.

Substitution of a group 5 metal for a tungsten atom in a polytungstate increases the overall negative charge of surface oxygens by one unit.^{8b} The increase in charge per surface oxygen/chalcogen atom for the more hydrolytically stable $[\text{PW}_{11}\text{O}_{39}\text{ME}]^{4-}$ (M = Nb, Ta; E = O, S, Se) is approximately half that for $[\text{W}_5\text{O}_{18}\text{ME}]^{3-}$. The opposite charge effect was reported for the hydroxide-catalyzed decomposition of the charged series $[\text{XW}_{12}\text{O}_{40}]^{n-}$ (X(n) = P(3), Si(4), B(5), H₂(6)).^{10,22} These previous studies concluded that increasing the negative charge of $[\text{XW}_{12}\text{O}_{40}]^{n-}$ decreased the rate of decomposition as a result of electrostatic repulsions between the polyoxoanion and the hydroxide anion. In this work, we observe that atom exchange or hydrolysis of the $\{\text{ME}\}^{3+}$ fragment in $[\text{PW}_{11}\text{O}_{39}\text{ME}]^{4-}$ is promoted by acid. The increased hydrolytic stability of $[\text{PW}_{11}\text{O}_{39}\text{ME}]^{4-}$ compared to $[\text{W}_5\text{O}_{18}\text{ME}]^{3-}$ can be rationalized by the lower surface charge density of the former if electrostatic attractions between a proton and the polyoxoanion are assumed to be important for its hydrolysis in dmf.

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Supporting Information Available: Text giving the preparation, elemental analyses, and IR data for the $[\text{PW}_{11}\text{O}_{39}\text{ME}]^{4-}$ (M = Nb, Ta; E = S, Se) and $[\text{NbW}_5\text{O}_{18}\text{Se}]^{3-}$ compounds, as well as a table of ¹⁸³W NMR data (3 pages). Ordering information is given on any current masthead page.

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(19) Preparation and analytical and characterization data for $[\text{NbW}_5\text{O}_{18}\text{Se}]^{3-}$ are found in Supporting Information.

(20) (a) ³¹P NMR of $[\text{PW}_{11}\text{O}_{39}\text{ME}]^{4-}$ (M = Nb, Ta; E = O, S, Se) (121.4 MHz, dmf): δ -12.7 (NbO), -13.6 (NbS), -13.8 (NbSe) ppm; -13.4 (TaO), -14.2 (TaS), -14.4 (TaSe) ppm upfield of 85% H₃PO₄(aq) external reference. (b) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 93.

(21) We observe that the terminal Nb oxo in $[\text{NbW}_5\text{O}_{19}]^{3-}$ exchanges readily at room temperature with 20 equiv of ¹⁷OH₂ in CH₃CN within 24 h as described in ref 2 and: Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.

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