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LETTER

Keggin polyoxotungstate derivatives containing technetium

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Heteropoly- and isopolyanions of the transition elements of Groups 5 and 6 constitute a large class of complexes [1] whose analogies to metal oxide surfaces [2] and potential and realized catalytic applications [3] provide current foci of attention. It is now also evident that these species possess biological activity as antiviral and antitumor agents [4]. In view of this latter application, it may prove useful to tag the polyoxoanions of interest with appropriate radionuclides to monitor the fate of the species for both *in vivo* and *in vitro* studies. Technetium is particularly attractive in this respect by virtue of the superior characteristics of ^{99m}Tc ($T_{1/2}=6$ h, 140 keV) for nuclear medicine imaging [5, 6] and of the availability of the relatively stable isotope ^{99}Tc which allows the development of technetium chemistry on a conventional analytical scale. Furthermore, the Group 7 congener rhenium is known to substitute for W(VI) atoms in polytungstates [7], suggesting that Tc incorporation into polytungstate cores is feasible.

We report here the synthesis and properties of a number of technetium-substituted polytungstates with the Keggin structure. The properties of these new heteropolyanions are compared to those of the previously reported $[PW_{11}ReO_{40}]^{4-}$ [7].

Experimental

Synthesis of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcO_{40}]$

A solution of $(n\text{-}C_4H_9)_4N[TcOCl_4]$ (100 mg, 0.2 mmol) in acetonitrile (2 ml) was added to a solution of $[(n\text{-}C_4H_9)_4H][H_3PW_{11}O_{39}]$ (0.6 g, 0.19 mmol) [8] in 5 ml of acetonitrile, resulting in an immediate color change to deep purple. After filtration, the solution was carefully layered with 5 ml of diethyl ether and allowed to stand for 2 days. The purple crystals of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcO_{40}]$ were filtered and washed with methanol. *Anal.* Calc. for $C_{64}H_{144}N_4O_{40}PTcW_{11}$: C, 20.4; H, 3.86; N, 1.49. Found: C, 20.5; H, 3.81; N, 1.48%. IR (KBr pellet, cm^{-1}): 2960(s), 2870(m), 1480(m), 1375(m), 1075(s), 960(vs), 880(s), 800(vs), 520(m), 375(m). UV–Vis (CH$_3$CN, λ_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1})): 38750 (20000), 24150 (400), 18900 (250, sh).

Synthesis of $[(n\text{-}C_4H_9)_4N]_5[SiW_{11}TcO_{40}]$

A solution of 100 mg (0.38 mmol) of Na[TcO(ethanediolate)$_2$] [9] in 2 ml of H_2O was added to a solution of 1.00 g (0.35 mmol) of α-$K_8SiW_{11}O_{39}\cdot12H_2O$ [10] in 10 ml of sodium acetate buffer, pH = 5.5. After stirring at 90 °C for 20 min, the dark solution was filtered and allowed to cool to room temperature. Addition of excess $(n\text{-}C_4H_9)_4NBr$ yielded a dark precipitate which was recrystallized from warm water to give dark purple crystals in 25% yield. *Anal.* Calc. for $C_{80}H_{180}N_5O_{40}SiTcW_{11}$: C, 24.0; H, 4.50; N, 1.75. Found: C, 23.7; H, 4.43; N, 1.69%. IR (KBr pellet, cm^{-1}): 2970(s), 2865(m), 1475(m), 1370(m), 1060(s), 955(vs), 870(s), 790(vs), 510(m), 390(m).

Synthesis of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcNO_{39}]$

A solution of 60 mg (0.12 mmol) of $[(n\text{-}C_4H_9)_4N][TcNCl_4]$ [11] in 2 ml of acetonitrile was added to a solution of 0.37 g (0.10 mmol) of $[(n\text{-}C_4H_9)_4N]_4[H_3PW_{11}O_{39}]$ in 10 ml of acetonitrile. The solution was filtered and allowed to stand at room temperature for 5 days, whereupon dark crystals of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcNO_{39}]$ formed. Yield: 20%. *Anal.* Calc. for $C_{64}H_{144}N_5O_{39}PTcW_{11}$: C, 20.6; H, 3.86; N, 1.88. Found: C, 20.4; H, 3.95; N, 1.72%. IR (KBr pellet, cm^{-1}): 2970(s), 2870(s), 1480(m), 1365(m), 1808(s), 1025(s), 950(vs), 880(s), 800(vs), 520(m), 380(m).

Fast atom bombardment mass spectroscopy

The positive and negative ion fast atom bombardment mass spectra (FAB-MS) were obtained using the first two sectors (MS-1) of a JEOL HX110/HX110 tandem double focusing mass spectrometer. The 6 keV neutral xenon primary beam was produced

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with a JEOL gun. The instrument was operated at 1:3000 resolution in the negative ion mode and 1:1000 resolution in the positive ion mode. Accelerating voltage was ±10 kV, and 18 kV postacceleration was applied at the detector. A sample of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcO_{40}]$ was dissolved in 1:1 DMSO/glycerol and 0.5 μl of this solution was applied to the stainless steel FAB target for each analysis.

Discussion

The monovacant Keggin derivatives of the type $[XW_{11}O_{39}]^{n-}$ form the largest and most versatile class of lacunary polyanions. The ligating ability of these polyanion structures has been recognized for many years [11] and has been exploited in the isolation of the complexes of this study. Since rhenium, the Group 7 congener of technetium is known to incorporate into Keggin structures [7], technetium appeared well suited for polyoxoanions by virtue of its appropriate radius and ability to form short terminal M=O bonds.

The reactions of appropriate Tc–oxo precursors with the lacunary polyoxotungstates $[XW_{11}O_{39}]^{n-}$ (X=P, Si) yield the Keggin derivatives $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcO_{40}]$ and $[(n\text{-}C_4H_9)_4N]_5[SiW_{11}TcO_{40}]$. The IR spectra of the Tc(V)-substituted anions are essentially indistinguishable from those of the corresponding $[XW_{12}O_{40}]^{n-}$ species, confirming the occupancy of the vacant site of the precursor lacunary species. The electronic spectrum of $[PW_{11}TcO_{40}]^{4-}$ in acetonitrile exhibits an oxygen to tungsten charge transfer at 38750 cm^{-1} and two weak bands at 24150 and 18900 cm^{-1} assigned as heteronuclear, Tc to W, intervalence charge transfer and d–d transitions. An analogous assignment has been made for $[PW_{11}ReO_{40}]^{4-}$ [7] where the greater intensity of these transitions suggests considerable intensity-enhancement. The bathochromic shift in the latter two bands of $[PW_{11}TcO_{40}]^{4-}$ when compared to the analogous bands in $[PW_{11}ReO_{40}]^{4-}$ is consistent with the relatively more facile reduction of technetium species than the corresponding rhenium complexes [12].

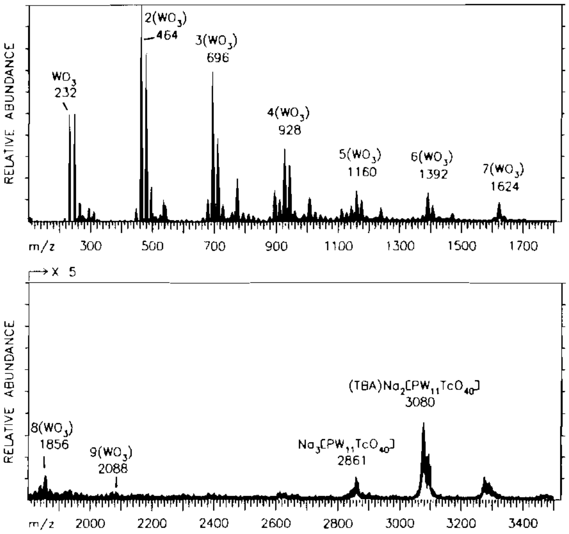

Fig. 1. Negative ion fast atom bombardment mass spectrum of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcO_{40}]$ in 1:1 DMSO/glycerol.

Fast atom bombardment mass spectrometry has been demonstrated to be a useful method for characterization of heteropolyanions, since it can provide both molecular weight information [13–15] and some structural detail [16]. These features are particularly important when, as in the case of the compounds described here, crystals suitable for X-ray analysis cannot be obtained. The negative ion fast atom bombardment mass spectrum of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcO_{40}]$ is shown in Fig. 1. It is dominated by the series $(WO_3)_n$, where $n=1$ to 9, and a second set of clusters that contain an additional oxygen atom. The highest mass ions in the negative ion spectrum form a series at 219 u intervals. These intervals represent exchanges of Na^+ (23 u) and Bu_4N^+ (242 u). The intact polyoxoanion has a charge of −4 and a weight of 2792 Da. Association with three sodium cations would give a net charge of (−1) and a mass of 2861, as observed. Exchange of one sodium cation for tetrabutylammonium (TBA) would yield the more abundant cluster centered around *m/z* 3080, and exchange of a second the *m/z* 3300 cluster, which is accompanied by a lower mass cluster (*m/z* 3278) in which a proton replaces one sodium. Higher mass clusters contain additional TBA groups. Sensitivity in the positive ion mode was much lower, as would be expected for polyoxoanions, but the spectrum did contain peaks in the *m/z* 3400–3800 range, which would indicate association of the anion with three or four TBA groups, as well as with sodium.

Although the complexes are electrochemically active, they display voltammetric characteristics significantly different from those observed for the analogous $[XW_{11}ReO_{40}]^{n-}$ species. Whereas $[PW_{11}ReO_{40}]^{4-}$ exhibits four reversible single electron processes corresponding to the Re based redox processes Re(III) ↔ Re(IV) ↔ Re(V) ↔ Re(VI) ↔ Re(VII), under similar conditions $[PW_{11}TcO_{40}]^{4-}$ displays a single reversible one electron oxidation at +0.84 V and a quasireversible reduction at −1.05 V (relative to Ag/AgCl) as shown in Fig. 2. Thus, the Tc center of $[PW_{11}TcO_{40}]^{n-}$ appears to exhibit only three accessible oxidation states: Tc(IV) ↔ Tc(V) ↔ Tc(VI), in contrast to the five oxidation levels accessible for the Re cluster.

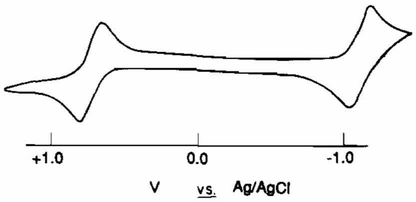

Fig. 2. Cyclic voltammogram of $[(n\text{-}C_4H_9)_4N]_4[PW_{11}TcO_{40}]$ in acetonitrile solution: 1.0×10^{-3} M in complex, 1.0 M $(n\text{-}C_4H_9)_4NPF_6$, Pt bead working electrode, Ag/AgCl couple reference.

The ligating ability of the lacunary polytungstates $[XW_{11}O_{39}]^{n-}$ may be further exploited in the isolation of clusters with strongly π-bonding groups other than the terminal oxo ligand occupying the sixth coordination position of the incorporated metal. In this fashion, the Tc–nitrido moiety may be introduced into the polytungstate core as illustrated by the complex $[PW_{11}TcNO_{39}]^{4-}$, in which the Tc center is apparently in the +6 rather than the +5 oxidation state. We are currently investigating the incorporation of Tc–hydrazido, Tc–diazenido and Tc–imido units into various lacunary types, such as $[XW_{10}O_{36}]^{n-}$, $[XW_9O_{34}]^{n-}$ and $[P_2W_{15}O_{56}]^{12-}$.

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