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Synthesis and Characterization of Tungstates Soluble in Nonaqueous Media

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Synopsis. A series of tungstates soluble in nonaqueous solvents were synthesized and characterized by elemental analyses and IR spectra. The heptameric compound $[(t\text{-}C_4H_9)NH_3]_6[W_7O_{24}]$ was structurally characterized by X-ray diffraction methods.

The chemistry of polyoxometalates, especially that of nonaqueous polyoxometalates, has been attracting increasing interest recently.[1—4] It has been demonstrated that plyoxometalates with novel stereochemistries can be synthesized by turning to nonaqueous solvents.[5—7] Many organometallic derivatives of polyoxometalate have been prepared in nonaqueous media during the last decade.[8]

The important key to this interesting yet unsurveyed field is the availability of a starting material that is soluble in organic solvents. Here we report the synthesis and characterization of a series of tungstates that are soluble in nonaqueous media.

Experimental

Reagents and Analytical Procedures. The following were purchased from commercial sources and used without further purification: Ethanol (Wako), acetone (Wako), H_2WO_4 (Wako), P_2O_5 (Wako), $(t\text{-}C_4H_7)NH_3$ (Tokyo Kasei). Elemental analyses were performed by Toray Research Center. Infrared spectra were recorded from mineral oil (Nujol) mulls between KBr plates on a Hitachi I-3000 spectrometer. Absorptions are described as follows: strong (s), medium (m), weak (w), broad (br), and shoulder (sh). The ^{183}W NMR spectrum of $[(t\text{-}C_4H_9)NH_3]_6W_7O_{24}\cdot 2H_2O$ was recorded at 16.66 MHz on a Varian Instruments UNITY plus 400 spectrometer. Chemical shift values were externally referenced to 2 M Na_2WO_4 solution (1 M=1 mol dm^{-3}) in D_2O by the sample replacement method.

Preparation of $[(t\text{-}C_4H_9)NH_3]_2(WO_4)$. H_2WO_4 (2.50 g, 10.0 mmol) was mixed with $(t\text{-}C_4H_7)NH_2$ (10.6 ml, 100 mmol), and 1 ml of deionized water was added dropwise to the mixture with vigorous stirring. After stirring the yellow suspension for 1 h, during which time it solidified, 10 ml of ethanol was added, and the mixture was further stirred for 2 h. The solid was collected by filtration, washed with 5 ml of ethanol, and dried under vacuum over P_2O_5 to yield 3.37 g of pale yellow product (8.50 mmol, 85.0% based on W). Anal. Calcd for $C_8H_{24}N_2WO_4$: C, 24.25; H, 6.12; N, 7.07; W, 46.4%. Found: C, 24.00; H, 6.26; N, 7.08; W, 46.8%. IR (Nujol, 1000—400 cm^{-1}; see Fig. 1.) 938 (w), 858 (m), 776 (s), 462 (m), 428 (w).

Preparation of $[(t\text{-}C_4H_9)NH_3]_6[W_7O_{24}]\cdot 2H_2O$. A solution of $[(t\text{-}C_4H_9)NH_3]_2(WO_4)$ (1.00 g, 2.52 mmol, in 40 ml of deionized water) was heated to boiling to reduce its volume to 10 ml. To this condensed solution, acetone was added to the point of saturation (ca. 65 ml). The mixture was heated briefly with a heat gun and the resulting clear solution was allowed to stand at ambient temperature. Block-shaped crystals appeared next day were collected by filtration and dried under vacuum over P_2O_5 for 24 h to yield 0.221 g of the product (0.104 mmol, 29.0%). Anal. Calcd for $C_{24}H_{76}N_6W_7O_{26}$: C, 13.40; H, 3.56; N, 3.91; W, 59.8%. Found: C, 13.21; H, 3.50; N, 3.92; W, 59.5%. IR (Nujol, 1000—400 cm^{-1}; see Fig. 1.) 946 (m), 908 (m), 878 (s), 828 (m), 722 (m), 660 (s), 576 (w), 482 (m), 454 (m). ^{183}W NMR (D_2O, 0.25 M, 16.66 MHz; see Fig. 2.) $\delta=269.4$ (1W, $\nu_{1/2}=1.0$ Hz), -91.1 (4W, $\nu_{1/2}=1.2$ Hz), -181.8 (2W, $\nu_{1/2}=1.8$ Hz).

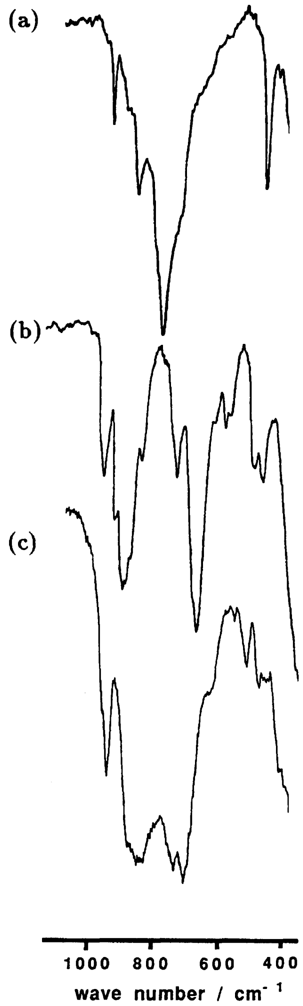

Fig. 1. IR spectra of (a) $[(t\text{-}C_4H_9)NH_3]_2(WO_4)$, (b) $[(t\text{-}C_4H_9)NH_3]_6[W_7O_{24}]\cdot 2H_2O$, and (c) $[(t\text{-}C_4H_9)NH_3]_{10}[H_2W_{12}O_{42}]$. See experimental section for numerical data.

Preparation of $[(t\text{-}C_4H_9)NH_3]_{10}[H_2W_{12}O_{42}]$. A solution of $[(t\text{-}C_4H_9)NH_3](WO_4)$ (1.00 g, 2.52 mmol, in 40

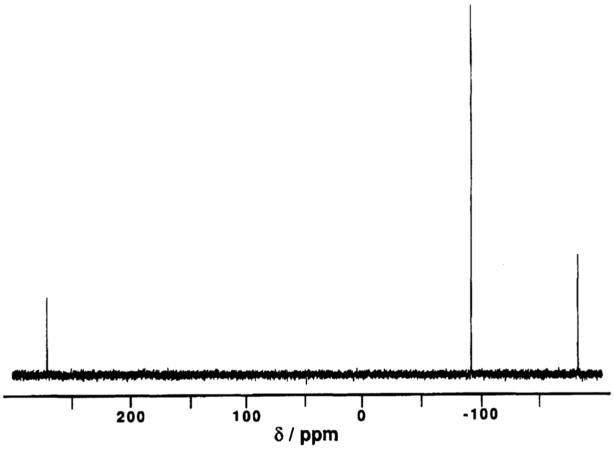

Fig. 2. ^{183}W NMR spectrum of $[(t\text{-}C_4H_9)NH_3]_6[W_7O_{24}]\cdot 2H_2O$ in D_2O. See experimental section for numerical data.

ml of deionized water) was heated to boiling and its volume was reduced to 10 ml. Acetone was added to this condensed solution to the point of saturation, and the mixture was heated briefly with a heat gun to obtain a clear solution. The solution was then allowed to stand at ambient temperature. Block-shaped crystals appeared the next day, but they changed into needle-like crystals on further standing. After 5 d all the block-shaped crystals had disappeared, and the needle-like crystals were collected by filtration to yield 0.285 g of the product (0.0783 mmol, 60.0%). Anal. Calcd for $C_{40}H_{126}N_{10}W_{12}O_{44}$: C, 13.13; H, 3.49; N, 3.83; W, 60.3%. Found: C, 12.83; H, 3.79; N, 3.76; W, 60.7%. IR (Nujol, 1000—400 cm^{-1}; see Fig. 1.) 930 (m), 838 (s, br), 722 (s), 692 (s), 610 (sh), 534 (w), 496 (m), 458 (m).

X-Ray Crystallographic Study of $[(t\text{-}C_4H_9)NH_3]_6[W_7O_{24}]\cdot 7H_2O$. Single crystals of $[(t\text{-}C_4H_9)NH_3]_6W_7O_{24}\cdot 7H_2O$ (formula weight 2241.92) suitable for X-ray diffraction studies were obtained as described above in the preparation section except that the final drying step had been omitted. The crystals are at 25±1 °C monoclinic, space group $P2_1/n$ with $a=13.961(9)$, $b=23.222(15)$, $c=18.278(9)$ Å, $\beta=101.53(2)$, $V=5806(6)$ Å^3, $Z=4$, $d_{calcd}=2.57$ g cm^{-3}. $R=0.060$ and $R_W=0.087$ for 5811 independent absorption-corrected reflections having $2\theta_{MoK\alpha}\leq 46.0°$ and $I\geq 3\sigma(I)$. The diffraction data were collected on an Enraf–Nonius CAD4 autodiffractometer, and the structure was solved by direct methods (MULTAN 82/11) and refined by full-matrix least-squares calculations (Enraf–Nonius SDP program package).[9] Tables of anisotropic thermal parameters, atomic coordinates, bond length and angles, and observed and calculated structure factors are deposited as Document No. 67048 at the Office of the Editor of Bull. Chem. Sco. Jpn.

Results and Discussion

Monomeric $[(t\text{-}C_4H_9)NH_3](WO_4)$ (**1**) was obtained by reacting H_2WO_4 directly with $(t\text{-}C_4H_9)NH_2$ in the presence of water. Attempts to crystallize the monomer, however, were unsuccessful. Addition of acetone to a concentrated aqueous solution of **1** did not yield crystals of the monomeric compound but yielded crystals of $[(t\text{-}C_4H_9)NH_3]_6[W_7O_{24}]$ (**2**) instead. The heptameric compound **2** was further converted to a dodecamer, $[(t\text{-}C_4H_9)NH_3]_{10}[H_2W_{12}O_{42}]$ (**3**), when its crystals were left in the water/acetone mixture for several days. The conversion can be followed by observing the crystal shapes. The crystals of the heptamer have a block-like shape, while those of the dodecamer are needle-like. All the compounds were characterized by elemental analyses and IR spectra. The IR spectrum of **2** showed a feature characteristic of Anderson-type (α-XM_6) polyoxometalates[10—12] (Fig. 1), although the anion in **2** actually has a Lindqvist-type (β-XM_6) structure[10—12] as discussed below. This again illustrates the danger of assigning a structure solely by IR spectra.[13]

The X-ray structural analysis of **2** revealed the presence of $(t\text{-}C_4H_9)NH_3^+$ cations, water molecules of crystallization, and discrete $[W_7O_{24}]^{6-}$ anions having the structure shown in Fig. 3. The $[W_7O_{24}]^{6-}$ anion has the same metal-oxygen framework as $[Mo_7O_{24}]^{6-}$.[10,14] Although it has no rigorous crystallographic symmetry, the anion approximates closely its maximum possible symmetry of $2m$ (C_{2v}). The same anion has also been found in $Na_6[W_7O_{24}]\cdot 21H_2O$[15] and $(C_5H_{10}NH_2)_6[W_7O_{24}]$.[16] The metal–oxygen bond lengths in the current compound are comparable to

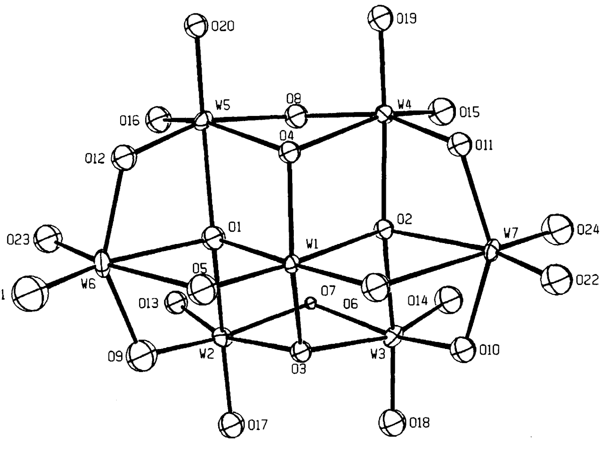

Fig. 3. ORTEP drawing of the $[W_7O_{24}]^{6-}$ anion. Ellipsoids and spheres are drawn to encompass 50% of the electron density. Selected distances (Å): W1–O1 2.26(2), W1–O2 2.26(2), W1–O3 1.89(2), W1–O4 1.89(2), W1–O5 1.75(3), W1–O6 1.79(3), W1–O1 2.20(2), W2–O3 2.31(2), W2–O7 1.94(2), W2–O9 1.99(3), W2–O13 1.75(3), W2–O17 1.74(2), W3–O2 2.27(2), W3–O3 2.26(2), W3–O7 1.94(2), W3–O10 1.99(2), W3–O14 1.73(3), W3–O18 1.70(2), W4–O2 2.07(2), W4–O4 2.24(2), W4–O8 1.98(2), W4–O11 1.96(2), W4–O15 1.74(3), W4–O19 1.73(2), W5–O1 2.14(2), W5–O4 2.32(2), W5–O8 1.92(2), W5–O12 1.97(2), W5–O16 1.78(3), W5–O20 1.73(2), W6–O1 2.17(2), W6–O5 2.50(3), W6–O9 1.90(3), W6–O12 1.90(2), W6–O21 1.74(3), W6–O23 1.75(3), W7–O2 2.22(2), W7–O6 2.45(2), W7–O10 1.92(2), W7–O11 1.88(2), W7–O22 1.75(3), W7–O24 1.75(3).

those found in $(RNH_3)[Mo_7O_{24}]\cdot 3H_2O$ (R=propyl, *iso*-propyl)[17] and $Na_6[W_7O_{24}]\cdot 21H_2O$.[15]

The anion of **2** seems to maintain its solid state structure in solution. The ^{183}W NMR spectrum of an aqueous solution of **2** (Fig. 2) showed three different peaks with a 1 : 4 : 2 intensity ratio, which is consistent with the structure shown in Fig. 3. A similar spectrum has been reported for a sodium salt of $[W_7O_{24}]^{6-}$.[15] Compound **2** is highly soluble in water, and a solution as concentrated as 0.25 M (1.75 M in total tungsten concentration) can be easily prepared. Concentrated aqueous solutions of **2** are stable and no $[(t\text{-}C_4H_9)NH_3]_{10}[H_2W_{12}O_{42}]$ precipitated out from the solution after 8 h. Concentrated aqueous solutions of $Na_6[W_7O_{24}]$, on the other hand, are unstable and usually $Na_{10}[H_2W_{12}O_{42}]$ crystallizes out from the solution within a couple of hours.[18,19]

Compounds **1**, **2**, and **3** are all readily soluble in methanol as well as in water. Compounds **2** and **3** are also soluble in dimethylsulfoxide. Thus they may serve as starting points for nonaqueous tungstate chemistry. In addition, the anions $[WO_4]^{2-}$, $[W_7O_{24}]^{6-}$, and $[H_2W_{12}O_{42}]^{10-}$ have relatively high negative charges per W atom, hence they are potentially good "molecular oxide supports" for organometallic compounds.

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