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Synthesis and structural characterization of new organotin derivatives of polyoxotungstates via transmetallation and coupling reactions

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Abstract

Organotin-substituted polyoxometalates $[WM(RSn)_2(MW_9O_{34})_2]^{10-}$; (M = Co, Zn; R = CH_3, C_2H_5, n-C_4H_9) have been prepared through exchange reaction of $[WM_3(H_2O)_2(MW_9O_{34})_2]^{12-}$ and the appropriate organotin trichloride in aqueous solution. The complexes have been characterized in solution by ^{183}W and ^{119}Sn NMR spectroscopy of the diamagnetic anions, and by single crystal structure determinations of salts of the methyl, ethyl and *n*-butyl derivatives of the tungstozincates and of the methyl derivative of a $CoZn_2$ analog. Cyclic voltammetry demonstrates for the first time for this class of polyoxometalates that the tetrahedral cobalt(II) centers are reversibly oxidizable to yield high-spin cobalt(III) analogs. Displacement of the kinetically metastable $[W_5O_{18}]^{6-}$ anion from $[Ce(W_5O_{18})_2]^{10-}$, by reaction with CH_3SnCl_3, leads to modest yields of $[CH_3SnW_5O_{18}]^{3-}$. Bis(trichlorostannyl)alkanes such as $Cl_3Sn(CH_2)_4SnCl_3$ can be used as covalent linkers of polyoxometalate anions to form the "dumbbell" complex $[SiW_{11}O_{39}Sn(CH_2)_4SnSiW_{11}O_{39}]^{10-}$ and linear oligomers $\{[(Sn(CH_2)_4Sn)(WZn(ZnW_9O_{34})_2)]^{10-}\}_x$.

Keywords: Polyoxotungstates; Organotin; NMR spectroscopy; X-ray crystallography; Di-tin linkers

1. Introduction

The synthesis of new types of polyoxometalates remains of current interest. In particular their applications in catalysis, as phasing agents for X-ray crystallography of very large biomolecules, and their potential medical applications attract much attention [1–4]. However, the full potential of polyoxometalate applications, their reaction mechanisms, and structural adaptability has not yet been developed and this encourages the pursuit of new structures, synthetic methodology, and reactivity patterns of these substances.

In view of the hydrolytic stability of tin–carbon (and germanium–carbon) bonds, and the comparable ionic radii of six-coordinate Sn (Ge) and W(VI), mono-organotin moieties provide a route to robust, water-stable organic derivatives of polyoxotungstates. The most frequently-used synthetic method involves the reaction of "tetrahedral" $RMCl_3$ with lacunary structures although the nucleophilic behavior of Sn(II)-substituted polyanions has also been shown to yield similar RSn^{3+} derivatives. as has direct assembly from tungstate and an appropriate heteroatom [5–16].

We now report that it is possible to replace labile metal cations embedded in polyoxotungstate structures with organotin groups. This opens up the rational synthesis of organic derivatives of polyoxoanions for which no stable lacunary anions are readily available. The use of α,ω-bis-(trichlorostannyl)alkanes, $Cl_3Sn(CH_2)_nSnCl_3$, to link polyoxometalate units is also briefly explored.

Recently, we have been interested in the chiral sandwich type polyoxometalates $WM\{M(H_2O)\}_2(MW_9O_{34})_2]^{12-}$ (M = Co or Zn) that were first reported by Tourné and Zonnevijlle [17,18]. The two aquated metal cations in the belt of this structure are labile and can easily be replaced by different transition metal cations [19–23]. We now show that an organotin moiety $\{RSn^{3+}\}$ can also replace the belt

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cations to form stable complexes with general formula $[WM(RSn)_2(MW_9O_{34})_2]^{10-}$ where M = Co or Zn and R = CH_3, C_2H_5, n-C_4H_9.

The di-tin precursors α,ω-bis-(trichlorostannyl)alkanes with general formula $Cl_3Sn(CH_2)_nSnCl_3$ have previously been reported for the synthesis of organotin-oxo clusters [24]. In this paper, we report the use of $Cl_3Sn(CH_2)_4SnCl_3$ as a new polyoxometalate linker by reacting it with $[SiW_{11}O_{39}]^{8-}$ to connect two lacunary POMs and also to form linear oligomers from $[WZn(Zn(H_2O))_2(ZnW_9O_{34})_2]^{12-}$.

Although the nonaqueous synthesis of $[PhSnW_5O_{18}]^{3-}$ and $[PhGeW_5O_{18}]^{3-}$ from $WO_4{}^{2-}$ and $PhMCl_3$ has been reported [25], we now show that reaction of $K_{10}[Ce(W_5O_{18})_2]$ and CH_3SnCl_3 yields $[CH_3W_5O_{18}]^{3-}$ in aqueous solution.

2. Experimental

The sodium salts of $[WM_3(H_2O)_2(MW_9O_{34})_2]^{12-}$ (M_5W_{19}) M = Co, Zn, $K_9[Ce^{III}(W_5O_{18})_2]\cdot nH_2O$ ($Ce(W_5)_2$) and $K_8[\alpha\text{-}SiW_{11}O_{39}]$ (SiW_{11}) were synthesized following published methods and identified by infrared spectroscopy and for Zn_5W_{19}, $Ce(W_5)_2$, and SiW_{11}, by ^{183}W NMR spectroscopy [17,18,26,27]. α,ω-Bis-(trichlorostannyl)butane ($Cl_3Sn(CH_2)_4SnCl_3$) was synthesized via α,ω-bis-(triphenylstannyl)butane [24,28]. Methyltintrichloride ($MeSnCl_3$), and butyltintrichloride ($BuSnCl_3$) (Aldrich) and ethyltintrichloride ($EtSnCl_3$) (Organometallics, Inc.) were used as supplied.

*$Cs_{10}[WZn(CH_3Sn)_2(ZnW_9O_{34})_2]\cdot 19.5H_2O$ (Cs_{10}**1**).* A solution of 5.0 g of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nH_2O$ (0.9 mmol) in 10 mL water was heated to 80 °C and added to a solution of 0.43 g of CH_3SnCl_3 (1.8 mmol) in 10 mL of water. The resulting mixture was stirred at 80 °C for 30 min, 2.25 mL of 4 M CsCl solution was added and the mixture stored in the refrigerator overnight. The solid product was filtered off and recrystallized from 15 mL of hot (90–95 °C) water by adding 1 mL of 4 M CsCl solution. The fine crystals were filtered off and air-dried overnight. Yield: 4.6 g (77%). *Anal.* Calc. for $C_2H_{45}Cs_{10}O_{87.5}Sn_2W_{19}Zn_3$: C, 0.36; Cs, 19.8; Sn, 3.53; W, 51.9; Zn, 2.9. Found: C, 0.39; Cs, 20.4; Sn, 3.70; W, 56.1; Zn, 3.0%. IR (metal oxygen stretching region): 1203, 935, 880, 751, 658 cm^{-1}.

*$Cs_{10}[Co(CH_3Sn)_2(CoW_9O_{34})_2]\cdot 20H_2O$ (Cs_{10}**2**), $Cs_{10}[WZn(CH_3CH_2\ Sn)_2(ZnW_9O_{34})_2]\cdot 15H_2O$ (Cs_{10}**3**)* and *$Cs_{10}[WCo(CH_3CH_2Sn)_2(CoW_9O_{34})_2]\cdot 14H_2O$ (Cs_{10}**4**)* were prepared in a similar fashion.

*Cs_{10}**2**.* Yield: 4.5 g (75%). *Anal.* Calc. for $C_2H_{46}Co_3Cs_{10}O_{88}W_{19}$: C, 0.36; Co, 2.63; Cs, 19.8; Sn, 3.54; W, 52.02. Found: C, 0.32; Co, 2.70; Cs, 19.6; Sn, 3.45; W, 54.8%. IR: 1203, 935, 885, 745, 660 cm^{-1}.

*Cs_{10}**3**.* Yield: 3.9 g (65%). *Anal.* Calc. for $C_4H_{40}Cs_{10}O_{83}Sn_2W_{19}Zn_3$: C, 0.72; Cs, 19.9; Sn, 3.6; W, 52.4; Zn, 2.9. Found: C, 0.67; Cs, 19.6; Sn, 3.73; W, 52.9; Zn, 3.2%. IR: 1192, 933, 884, 750, 658, 539 cm^{-1}.

*Cs_{10}**4**.* Yield: 3.6 g (60%). *Anal.* Calc. for $C_4H_{38}Co_3Cs_{10}O_{82}Sn_2W_{19}$: C, 0.72; Co, 2.7; Cs, 20.0; Sn, 3.6; W, 52.5. Found: C, 0.71; Co, 2.8; Cs, 20.3; Sn, 3.7; W, 55.1%. IR: 1190, 934, 883, 857, 751, 655, 538 cm^{-1}.

*$Cs_{10}[WZn(C_4H_9Sn)_2(ZnW_9O_{34})_2]\cdot 18H_2O$ (Cs_{10}**5**)* was prepared using the same procedure and quantity as above except that before and during the addition of the solution of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ to the $C_4H_9SnCl_3$ the temperature was maintained at ca. 40 °C. After 5 min the temperature was slowly raised to 80 °C and kept there for 30 min. Yield: 3.0 g (50%). *Anal.* Calc. for $C_8H_{54}Cs_{10}O_{86}Sn_2W_{19}Zn_3$: C, 1.42; Cs, 19.6; Sn, 3.50; W, 51.5; Zn, 2.9. Found: C, 1.52; Cs, 19.4; Sn, 3.56; W, 51.9; Zn, 2.9%. IR: 1167, 1086, 936, 879, 752, 657, 600, 535 cm^{-1}

*$Cs_{10}[WCo(C_4H_9Sn)_2(CoW_9O_{34})_2]\cdot 17H_2O$ (Cs_{10}**6**)* was prepared using the same procedure used for **5**. Yield: 3.4 g (57%). *Anal.* Calc. for $C_8H_{52}Co_3Cs_{10}O_{85}Sn_2W_{19}$: C, 1.43; Co, 2.62; Cs, 19.7; Sn, 3.52; W, 51.8. Found: C, 1.45; Co, 2.71; Cs, 19.8; Sn, 3.63; W, 53.2%.

*$Cs_{10}[WCo(CH_3Sn)_2(ZnW_9O_{34})_2]\cdot 20H_2O$ (Cs_{10}**7**).* To 20 mL of a warm solution (80 °C) of $Co(NO_3)_2\cdot 6H_2O$ (2.16 g, 9.1 mmol) was added 10 mL of a solution of $MeSn_2Zn_3W_{19}$ (10.5 g, 1.8 mmol). The solution changed color from pink to reddish brown and the resulting mixture was heated to near boiling for 2 h. The solution was then allowed to cool and passed through a cation exchange column (K^+) to remove excess unreacted cobalt. The eluate had a reddish green color. CsCl solution (4 M) was added to obtain a solid which was then recrystallized from the minimum amount of hot water (yield 6.5 g, 62%). *Anal.* Calc. for $C_2H_{46}CoCs_{10}O_{88}W_{19}Zn_2$: C, 0.36; Co, 0.88; Cs, 19.8; Sn, 3.53; W, 52.0. Found: C, 0.39; Co, 0.91, Cs, 20.2; Sn, 3.21; W 53.3%.

The isostructural but *achiral analogs* of **1**, **3** and **5**, $[(RSn)_2Zn_2(PW_9O_{34})_2]^{8-}$ (R = Me, Et, n-Bu) were also prepared for spectroscopic comparisons, see below and in Supplementary material.

*$K_{10}[SiW_{11}O_{39}Sn(CH_2)_4SnSiW_{11}O_{39}]\cdot H_2O$ (**8**).* In 40 mL of DMF $Cl_3Sn(CH_2)_4SnCl_3$ (0.47 g, 0.93 mmol) and SiW_{11} (6 g, 1.9 mmol) were mixed and the slurry was heated at 100 °C overnight. The solution was filtered hot and 5 mL of a saturated solution of KCl was added first, followed by ethanol to yield a solid product which was recrystallized from the minimum of water. Yield: 5.4 g (90%).

Samples containing *$[(SnC_4H_8Sn)_{2n}\{WZn(ZnW_9O_{34})_2\}_n]^{10n-}$ (**9**)* were prepared as follows. A solution of $Cl_3SnC_4H_8SnCl_3$ (0.91 g, 1.8 mmol) in 40 mL of DMF was treated with solid Zn_5W_{19} (5 g, 0.9 mmol) and the slurry was heated at 100 °C overnight. After filtration to remove undissolved material, ethanol was added to precipitate 4.5 g (90%) of product.

2.1. Physical measurements

Infrared spectra were recorded in KBr pellets on a Spectrum One FT-IR spectrometer (Perkin–Elmer Instruments)