J. Am. Chem. Soc. **2001,** *123,* 2087−2088

Formation of Unsymmetrical Polyoxotungstates via Transfer of Polyoxometalate Building Blocks. NMR Evidence Supports the Kinetic Stability of the Pentatungstate Anion, $[W_5O_{18}]^{6-}$, in Aqueous Solution

Nebebech Belai, Masahiro Sadakane, and Michael T. Pope*

Department of Chemistry, Box 571227
Georgetown University, Washington, D.C. 20057-1227

Received September 5, 2000

Current interest and activity in polyoxometalate chemistry is driven by the enormous range of composition, structure, and properties exhibited by these complexes.[1] Most large polyoxometalate anions have structures which can be viewed as assemblies of smaller polyoxometalate building blocks. Especially common are polyoxotungstates incorporating so-called lacunary anions, e.g. $[U(GeW_{11}O_{39})_2]^{12-}$,[2] $[\{Co(H_2O)\}_3(PW_9O_{34})_2]^{12-}$,[3] and $[(WO_2)_4(AsW_9O_{33})_4]^{28-}$,[4] but structures based on complete ("plenary") anions are also known, e.g. $[Mn(Nb_6O_{19})_2]^{12-}$ [5] and $\{[Th(H_2O)_3(UMo_{12}O_{42})]^{4-}\}_\infty$.[6]

In all the above examples the polyanion subunits are independently stable and can be isolated in the form of crystalline salts. In many cases the composite anions have been synthesized directly from the preformed components. To explore the possibility of directed synthesis of unsymmetrical or very large polyoxometalate species via assembly of appropriate subunits we are investigating interanion transfer of such blocks.

The Peacock−Weakley anions $[M(XW_{11}O_{39})_2]^{n-}$ and $[M(X_2W_{17}O_{61})_2]^{m-}$ may be viewed as 8-coordinate complexes (square anti-prism geometry) of lanthanide or actinide(IV) cations, M, with tetradentate lacunary polyoxotungstate "ligands".[7−9] Solutions of these complexes in the presence of free ligand show that ligand exchange is slow on the NMR time scale.[10] The same M-cations also form a series of decatungstometalates $[M(W_5O_{18})_2]^{n-}$ with analogous structures,[7a,11,12] but in this case the ligand, which is a lacunary derivative of the hexatungstate anion $[W_6O_{19}]^{2-}$, has never been characterized as an independent species. The hexatungstate ion itself is stable only in nonaqueous solution. Consequently the decatungsto complexes, as well as a handful of other species incorporating $\{W_5O_{18}\}$ groups,[13] have been synthesized starting from aqueous monotungstate solutions.

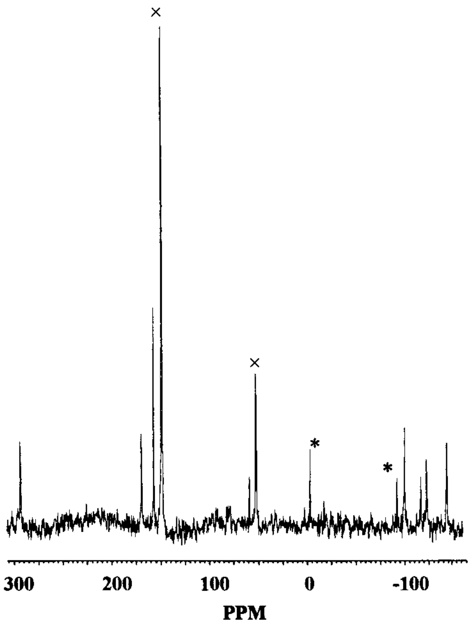

Figure 1. ^{183}W spectrum (12.5 MHz) of a mixture of 25 mM PW and 75 mM $Ce(W_5)_2$ showing the presence of $Ce(PW)(W_5)$ (unmarked peaks), excess $Ce(W_5)_2$ (×), and residuals of displaced "W_5" (*).

Phosphorus-31 NMR spectra of aqueous solutions containing mixtures of $[Ce^{III}(PW_{11}O_{39})_2]^{11-}$ ($Ce(PW)_2$) and $[Ce^{III}(W_5O_{18})_2]^{9-}$ ($Ce(W_5)_2$) show, in addition to the signal at −18.0 ppm from $Ce(PW)_2$, a peak at −23.6 ppm that can be tentatively attributed to the mixed anion $[Ce^{III}(PW_{11}O_{39})(W_5O_{18})]^{10-}$ ($Ce(W_5)(PW)$).[14] The same signal is observed in solutions containing mixtures of $[PW_{11}O_{39}]^{7-}$ (PW, $\delta_P = -10.2$) and $Ce(W_5)_2$, and is the only phosphorus-containing species present when the molar ratio $Ce(W_5)_2$/PW = 3. The ^{183}W NMR spectrum of such a mixture is shown in Figure 1 and reveals all the signals expected for $Ce(W_5)(PW)$ and for unreacted $Ce(W_5)_2$ according to the stoichiometry

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* Address correspondence to this author.

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(14) Potassium salts of PW, $Ce(PW)_2$, $Ce(W_5)_2$, and the corresponding La derivatives were prepared by literature methods[7a] and identified by NMR spectroscopy (Table 1: Fedotov, M. A.; Samokhvalova, E. P.; Kazansky, L. P. *Polyhedron* **1996**, *15*, 3341−3351. Sveshnikov, N. N.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 591−594). Phosphorus-31 NMR spectra were recorded in 5-mm tubes on a Varian Mercury 300 MHz spectrometer (operating at 121.47 MHz). 85% H_3PO_4 was used as an external reference for all spectra. Tungsten-183 spectra were recorded in 10-mm tubes on a Bruker AM-300 spectrometer (12.505 MHz for ^{183}W). 2 M Na_2WO_4 was used as an external standard for all spectra. Potassium salts of $Ce(W_5)_2$ and PW were converted to the more soluble lithium salts by treatment with $LiClO_4$ solution, followed by removal of insoluble $KClO_4$.

10.1021/ja005578n CCC: $20.00

Table 1. NMR Chemical Shifts

anion	^{31}P	^{183}W
$[PW_{11}O_{39}]^{7-}$	−10.2	−95.8, −97.0, −102.0, −119.6, −130.8, −150.5
$[Ce^{III}(H_2O)_x(PW_{11}O_{39})]^{4-}$	−20.5	324.2, 171.7, −100.7, −113.6, −119.7, −140.9
$[Ce^{III}(PW_{11}O_{39})_2]^{11-}$	−18.0	355.2, 196.5, −99.3, −115.1, −117.2, −141.8
$[Ce^{III}(W_5O_{18})_2]^{9-}$		149.1 (4W), 51.5 (W)
$[Ce^{III}(PW_{11}O_{39})(W_5O_{18})]^{10-}$	−23.6	292.6, 168.8, −100.6, −117.2, −123.7, −144.6, 156.8, 58.4

$$[PW_{11}O_{39}]^{7-} + 3[Ce^{III}(W_5O_{18})_2]^{9-} \rightarrow [Ce^{III}(PW_{11}O_{39})(W_5O_{18})]^{10-} + 2[Ce^{III}(W_5O_{18})_2]^{9-} + \text{“}[W_5O_{18}]^{6-}\text{”}$$

The ultimate fate of the displaced pentatungstate ligand is not yet determined.[15] As shown in Table 1 the W NMR signature of Ce(W_5)(PW) is clearly distinguishable from those of Ce$(PW)_2$ and $[Ce^{III}(H_2O)_x(PW_{11}O_{39})]^{4-}$ (Ce(PW)).[16] The eight-line W NMR spectrum of Ce(W_5)(PW) (two and six lines for coordinated W_5 and PW_{11} ligands respectively) demonstrates that the CeO_8 antiprism is rotationally fluxional, as is the case for other Peacock−Weakley anions.[17]

The initial experiments demonstrate the formation of unsymmetrical (mixed “ligand”) species by interanion transfer of PW, presumably through dissociation of Ce$(PW)_2$ into PW and Ce(PW), both of which are stable in aqueous solution.[18] The question of the transferability of the pentatungstate ligand was addressed as follows. The lanthanum(III) analogue of Ce(W_5)(PW) was identified by a P NMR signal at −11.4 ppm in mixtures of PW and La$(W_5)_2$. The chemical shift for La$(PW)_2$ is −11.3. Figure 2 shows the P NMR spectrum of a 1:1 molar mixture of Ce$(PW)_2$ and La$(W_5)_2$ which shows the presence of La$(PW)_2$, La(W_5)(PW), Ce$(PW)_2$, and Ce(W_5)(PW) in approximately equal amounts. While La(W_5)(PW) could have been formed by the transfer of PW to La$(W_5)_2$, the formation of Ce(W_5)(PW) can only have resulted from transfer of the $[W_5O_{18}]^{6-}$ free ligand. This result demonstrates that both the pentatungstate anion and complexes such as $[Ce(H_2O)_x(W_5O_{18})]^{3-}$ have kinetic stability in aqueous solutions. The implications for the controlled self-assembly synthesis of new multi-unit polyoxoanions with desired shapes and properties are highly encouraging.

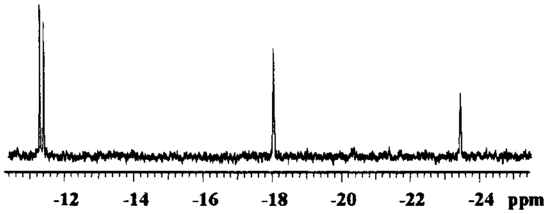

Figure 2. Phosphorus-31 NMR spectrum of an equimolar mixture of La$(W_5)_2$ and Ce$(PW)_2$. The four peaks shown correspond, from left to right, to La$(PW)_2$, La(PW)(W_5), Ce$(PW)_2$, and Ce(PW)(W_5), repectively.

Acknowledgment. We thank the National Science Foundation (CHE-9727417) and Mitsubishi Chemical Corporation for support.

JA005578N

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[15] In all mixing experiments in which “W_5O_{18}” was displaced, new reproducible W NMR signals were observed at −4.4, −18.0, −92.9, and −179.8 ppm. Whether these belong to one or more species is currently under investigation.

[16] The ammonium salt of Ce(PW) was prepared in 72% yield (based on W) according to a previously described method [Sadakane, M.; Dickman, M. H.; Pope, M. T. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2914−2916]. Elemental Anal. Found (Calcd for $(NH_4)_4[Ce(PW_{11}O_{39})]\cdot 10H_2O\cdot 1.5NH_4Cl$); N, 2.13 (2.45); H, 1.08 (1.34); Ce, 4.14 (4.45); P, 0.89 (0.98); W, 64.22 (64.20); Cl, 1.72 (1.69). IR: 1097, 1047, 958, 881, 837, 775, 704 cm^{-1}.

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