INORGANIC CHEMISTRY – QUALIFYING EXAM **06/17/2008**

The questions are based on the following article:

Graham and Finke, **The Classic Wells-Dawson Polyoxometalate, $K6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$: Answering the 88 Year-Old Question of What is Its Preferred, Optimum Synthesis?**

Inorg. Chem. **2008**, *47*, 3679.

(1) What is the basic difference between the Wells-Dawson and the Keggin forms of the phosphotungstate polyoxometalate ion (no drawing, just basic stoichiometry). (**1 point**)
The authors mention the formation of a themodinamically less favored β-isomer in the paper. What is the basic difference between the α and β-isomers, and based on that how would you explain their different ^{31}P NMR spectra? (**1 point**)

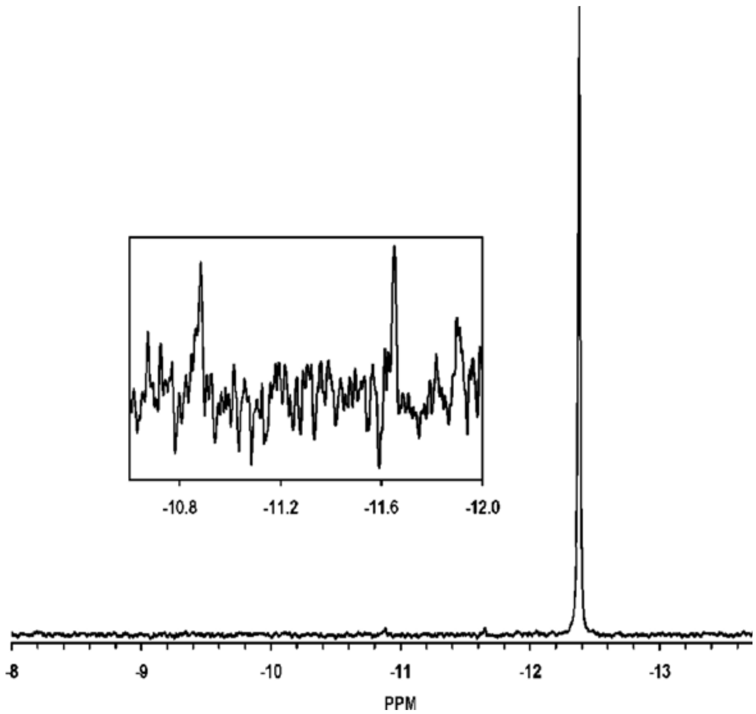
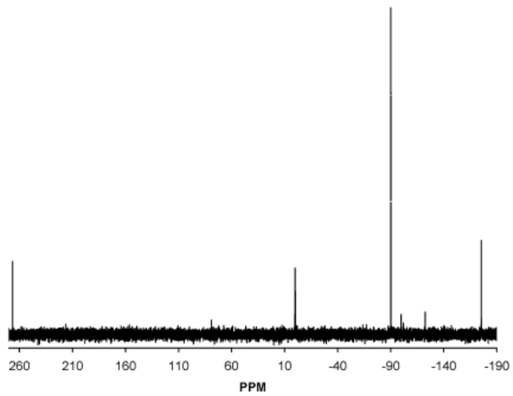


Figure1. ^{31}PNMR of $K6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$ (purity ≥ 97%) from Nadjo synthesis. The α-isomer peak is shown at –12.3 ppm. Small β-isomer impurity peaks can be seen around –10.8 and –11.6 ppm.

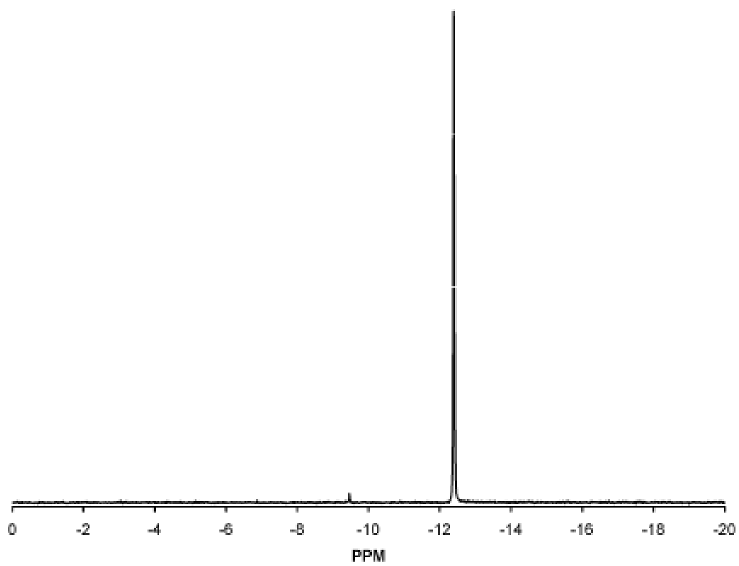
(2) Name the polyoxometalate byproducts that formed during the reaction (the ^{31}P NMR signals of these compounds can be found even in the spectrum (3B) of the purified product). One of these byproducts is, in fact, a follow up product of the desired compound. What was the reason for the formation of this byproduct in the D-R-F procedure, and how did the authors solve the problem? **(2 points)**

(3) Multinuclear NMR is a very important method for the state of the art identification of inorganic compounds as well. There are about 120 nuclei in the Periodic Table, that are applicable for NMR studies.

- What is the basic requirement for a nucleus to be NMR active? Briefly explain why the ^{31}P is one of these nuclei? (**2 points**)
- Analyze the following spectra:



(A) The ^{183}W NMR spectrum of the Nadjo product. Identify the peaks (with the parent compound). (**2 points**)



(B) The ^{31}P NMR spectrum of the 99% pure D-R-F product. Identify the peaks, including the minor ones (with the parent compound).

(2 points)

Green Chemistry: **(2 points)**

Based on the Table provided below and your own analysis of the paper, identify the preparation method for the target compound that is the least harmful to the environment.

Table 2. Moles of Reagents Used and Product Formed in the Synthesis of $[P_2W_{18}O_{62}]^{6-}$ as well as the Minimum Moles Required for the Stoichiometry Given in Footnote *a*

synthesis	$Na_2WO_4 \cdot 2H_2O$	H_3PO_4	HCl	NH_4Cl	KCl	$KHCO_3$	$[P_2W_{18}O_{62}]^{6-}$ [c]
ideal, minimum moles required [a]	*0.91*	*0.10*	*1.52*	*0.30*	*0.30*	*0.00*	*0.05*
(1) Wu [b]	0.91	3.64	0.00	14.96	0.00	0.00	0.01 [d]
(2) Souchay [b]	0.91	6.64	0.00	11.22	0.00	0.00	? [e]
(3) Droege thesis [b]	0.91	6.64	1.98	0.0	8.05	1.95	0.04
(4) Contant [b]	0.91	3.70	0.00	2.80	1.04	0.00	0.04
(5) D-R-F	0.91	6.64	1.26	0.00	7.71	1.10	0.04
(6) Nadjo	0.91	1.00	1.00	0.00	2.00	0.00	0.05

[a] Atom economy (minimum mole amounts) are given according to the following stoichiometry: $18[WO_4]^{2-} + 2H_3PO_4 + 30H^+ + 6(K^+ \text{ or } NH_4^+) \rightarrow (K \text{ or } NH_4)_6[P_2W_{18}O_{62}] + 18H_2O$. [b] The actual mole amounts of $Na_2[WO_4] \cdot 2H_2O$ in Wu's, Souchay's, Contant's and Droege's syntheses are 0.61, 0.61, 0.76, and 0.30, respectively. The scale, and thus moles of all reagents and products, of Wu's, Contant's and Droege's syntheses have each been increased proportionately to equal that of the other two larger scale syntheses for comparison. [c] Yield is based on 300 g of $Na_2WO_4 \cdot 2H_2O$. [d] Wu quantitated only $[\beta\text{-}P_2W_{18}O_{62}]^{6-}$. [e] Souchay did not quantitate his products.