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Organophosphonotungstic HPA of Keggin Type with Sulfo, Taurine and Glycine Substituted Ethylphosphonic Acids as the Coordinate Center

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Abstract: The title compounds **2a–c** were synthesized and characterized for the first time. Their proton numbers are around 3.2 ± 0.15 and are not in proportion with the valid acidity-basicity of the central phosphonic acids. The entirety of phosphonic acids **1a-c** is as the coordinate center of heteropoly anions of **2a–c**.

Keywords: Sulfoethylphosphonic acid, taurine, glycine, substituted ethylphosphonic acid, heteropoly acids, organophosphonotungstic heteropoly acids, Keggin type, synthesis.

Recent years, heteropoly acids （HPA）and their derivatives have received current attention due to their potential applications in analytical chemistry, catalysis, material sciences and medicine[1-2]. Usually, the core or coordinate center for most of the heteropoly compounds (HPC) are inorganic acids such as H_3PO_4, H_3SiO_3 *etc.* Although HPC with organophosphonic acids as coordinate center have been confirmed about 15 years ago, in which the molar ratio x: m for most of the heteropoly anions $[(RPO_3^{2-})_x M_mO_y]^{q-}$ (M=W, Mo, V…) are 4:4, 2:6, 8:12, 2:11, 1:6, 1:7. The coordinate center of the HPA of the Keggin type structure that their heteropoly anions with the P:M molar ratio 1:12 are still inorganic phosphoric acids[3]. No HPA of the Keggin type structure with organophosph- onic acids as the coordinate center has been reported until last year. We reported the synthesis and characterization of the HPA of Keggin type structure with β-aminoethylphosphonic acid (β-AEPA) and its N-substituted derivatives $RR'NCH_2CH_2PO_3H_2$ as the coordinate center for the first time[4].

Our research reveals that the new type of organophosphonotungstic HPA of the Keggin structure could be synthesized with β-AEPA and its N-substituted derivatives as the coordinate center of the heteropoly anions. Therefore we deduced，it is the organic side chain $RR'NHCH_2CH_2$- which contains nitrogen atom, who plays coordinating act as another hydroxy group of the phosphoric acid H_3PO_4. In other words, the entirety of each the organophosphonic acids $RR'NCH_2CH_2PO_3H_2$ like the inorganic phosphoric acid，act as the coordinate center of the organoph- osphonotungstic heteropoly anions of the Keggin type structure with the P:W molar ratio 1:12.

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The organophosphonic acids such as cyclohexyl phosphonic acid $C_6H_{11}—PO_3H_2$ which didn't contain nitrogen atom in their organic side chain will not form HPA of Keggin type structure with the P:M molar ratio 1:12, as the result summed up by our predecessors[3].

We report in this paper the synthesis and characterization of Keggin type of organophosphono-tungstic HPA **2a-c** with sulfo, taurine and glycine substituted ethyl-phosphonic acids as the coordinate center. The preparation equation is as following:

$$G—CH_2CH_2PO_3H_2 \xrightarrow[H^+]{NaWO_4\ 2H_2O} G—CH_2CH_2PO_3H_2 \cdot W_{12}O_{36} \cdot nH_2O$$

1a-c **2a-c**

	1a-c		**2a-c**	**G**
1a	SEPA	**2a**	SEPA-HPW	$-SO_3H$
1b	SEAEPA	**2b**	SEAEPA-HPW	$-NHCH_2CH_2SO_3H$
1c	CMAEPA	**2c**	CMAEPA-HPW	$-NHCH_2COOH$

Experimental

Bio-Rad FTS-185 IR, UV-VIS 8500 spectrophotometer, PE TGA7-DSC7 thermal-analysis instru- ment, PE 2400 CHN automatic instrument, LP8410 ICP instrument, D/MAX-3C full-automatic XRD instrument (Cu target, V=40KV, I=30Ma) were used. The material organophosphonic acids **1 a-c** were synthesized by the reaction of $ClCH_2CH_2PO_3H_2$ with Na_2SO_3, $H_2NCH_2CH_2SO_3H$, H_2NCH_2COOH respectively, according to the procedure described in ref 5. All the reagents including the $H_3PW_{12}O_{40} \cdot nH_2O$ (**PW_{12}**) were A R grade.

The title compounds **2a -c** were prepared as the procedure described in ref 4, and were char- acterized by means of IR , UV , elemental analysis, XRD, XPS, TG and DSC thermal analysis.

Results and Discussion

The characteristic peaks of IR spectra of the inorganic **PW_{12}**, **AEPA-HPW** ($H_2NCH_2CH_2$- $PO_3H_2 \cdot 12WO_3 \cdot nH_2O$)[5], **2a–c** are given in **Table 1**, and the UV spectra of the aqueous solution and ethanol solution of them are given in **Table 2**. The IR spectra of **2b** and UV spectra of ethanol solution for **2a** are shown in **Figure 1** and **Figure 2** respectively.

The 4 main characteristic peaks of IR spectra for PW_{12} of Keggin type structure are 1080, 982, 891, 796 cm^{-1}; the corresponding 4 main characteristic peaks of IR spectra for $H_4P_2W_{18}O_{42} \cdot nH_2O$ of Dawson type are 1091, 962, 913, 779 cm^{-1}; for PW_9 are 1052、941、836、740-760 cm^{-1}; and the P-O stretch peak of IR spectra for PW_{11} of defect Keggin type structure would split into two peaks of 1084 and 1038 cm^{-1}. The IR and UVspectra of the title compounds **2a–c** are as analogous as that of the Keggin structure inorganic **PW_{12}**, only with a little difference which was caused by the different organo-phosphonic acid and different number of crystal water. Usually, the primary structure of the HPA was confirmed by IR and UV spectra. The IR and UV spectra data indicated that the primary structure of the title compounds **2a–c** is Keggin type, the same as that of **PW_{12}** and **AEPA-HPW**.

The 2 θ angles of XRD for the title compounds **2a–c** are around 7-10°, 16-22°, 25-30°, 33-38° respectively, which are analogous to that of the XRD characteristic peaks of typical heteropoly anion of Keggin structure **PW_{12}** with little difference of the location and strength of the peaks, due to the different organic side chain of the phosphonic acid and different number of crystal water of **2a–c**.

Table 1 The IR data for $\mathbf{PW_{12}}$, **AEPA-HPW** and **2a–c** (ν in cm^{-1})

Sample	ν	$\nu(P-O_a)$	$\nu(W{=}O_d)$	$\nu(W\text{-}O_b\text{-}W)$	$\nu(W\text{-}O_c\text{-}W)$	ν	ν
$\mathbf{PW_{12}}$	3378	1080	982	891	796	595	524
AEPA-HPW	3381	1080	982	888	799	595	523
2a	3370	1081	983	892	797	595	524
2b	3391	1080	983	890	798	595	522
2c	3387	1081	983	891	797	595	524

Table 2 The UV spectra data for $\mathbf{PW_{12}}$, **AEPA-HPW** and **2a–c** (nm)

Sample	$O_d \rightarrow W$ / $O_{b,c} \rightarrow W$(in H_2O)		$O_d \rightarrow W$/ $O_{b,c} \rightarrow W$(in ethanol)	
$\mathbf{PW_{12}}$	200	256	209	266
AEPA-HPW	199	256	209	266
2a	196	257	209	266
2b	198	256	209	266
2c	196	257	212	266

Figure 1 The IR spectra of **2b**

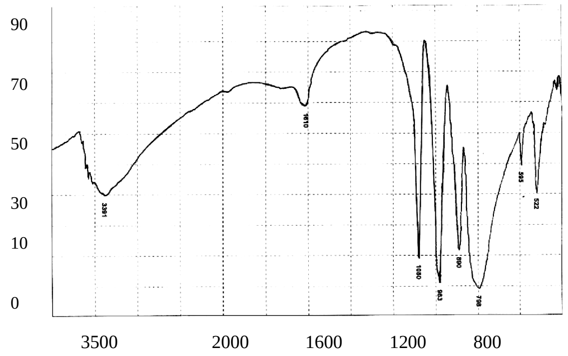
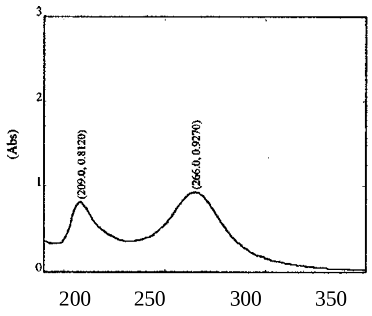


Figure 2 The UV spectra in EtOH for **2a**



The composition of the title compounds **2a–c** are $[G\text{-}CH_2CH_2PO_3H_2 \bullet 12WO_3] \bullet nH_2O$ with 1:12 of P / W ratio. The TG-DCS thermo-analysis curves of the title compounds **2a-c** are quite similar to that of $\mathbf{PW_{12}}$ and **AEPA-HPW**. Their TG curves possess three inflection points which imply the three stages of the dehydration: the loss of zeolite water, combination water and structure water or composition water respectively. Finally, above 530°C, the HPA samples were gradually decomposed into water, oxides of phosphorus and tungsten. **Table 3** gives the corresponding temperatures and numbers of dehydration for the lost weight of the first three steps and the numbers of crystal water n for **2a-c**.

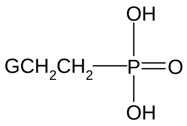
From the data in **Table 3**, the thermal stability for **2a–c** are close to inorganic $\mathbf{PW_{12}}$ and **AEPA-HPW**, and **2a** possessed higher thermo-stability than the others. The total process of the dehydration and decomposition for **2a-c** could be described in the same way as that of the first group of organophosphonotungstic HPA of Keggin type structure[4].

$$[H_5O_2^+]_3 \bullet G\text{-}CH_2CH_2PO_3^{2-} \bullet 12WO_3 \bullet xH_2O \rightarrow [H_5O_2^+]_3 \bullet G\text{-}CH_2CH_2PO_3^{2-} \bullet 12WO_3 \rightarrow G\text{-}CH_2CH_2PO_3H_2 \bullet 12WO_3 \rightarrow PW_{12}O_{37.5} \rightarrow 1/2\ P_2O_3\ +12\ WO_3$$

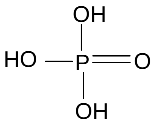
Table 3 Temperatures T and numbers of dehydration m and crystal water n of **2a-c**

Sample	T_1	m_1	T_2	m_2	T_3	$n = m_1 + m_2$
PW_{12}	101.5	15.1	214.9	6.2	370-508	21.3
AEPA-HPW	94.3	9.7	220.6	6.9	366-520	16.7
2a	118.5	18.1	223.2	6.2	357-558	24.3
2b	99.4	9.5	202.8	6.6	399-497	16.1
2c	103.2	16.1	214.3	6.5	382-521	22.6

Comparing with $H_2O_3PCH_2CH_2NH_2$ β-AEPA，**1a** contains acidic group G =—SO_3H but no nitrogen atom; **1b** and **1c** contains one more strong or weak acidic group G =—$NHCH_2CH_2SO_3H$ or -$NHCH_2COOH$. By pH titration with KOH-C_2H_5OH and calculation, the proton numbers for **WP_{12}**, **AEPA-HPW** and **2a-c** are 3.32, 3.24, 3.34, 3.28 and 3.05 respectively, which was implied that the proton number of organophosphonotungstic HPA is not in proportion with the valid acidity-basicity of the central organophosphonic acids. Obviously the structure of heteropoly anion of the title compounds **2a-c** is also Keggin type which is similar to that of the first group of Keggin type structure of organophosphonotungstic HPA[5]. The -PO_3H_2 group and the organic side chain G-CH_2CH_2- both participate in the formation of the primary structure of heteropolyanions of the title compounds **2a–c**. In other words, the organic side chain connected with the phosphono group and occupied the position of -OH group of phosphoric or phosphonic acids.



$$GCH_2CH_2-P(=O)(OH)_2$$



$$HO-P(=O)(OH)_2$$

The synthesis and characterization of title compounds **2a-c** enrich the research of organopho- sphonotungstic HPA. The research field of organophosphonotungstic HPA can be extended from nitrogen-containing organophosphonic acids to sulfur and oxygen-containing organophosphonic acids; from β-AEPA and its N-substituted derivatives, the one nitrogen atom-containing organophosphonic acids to poly hetero atom-containing organophosphonic acids; from basic group-containing organophosphonic acids to acidic group-containing, amino acid-containing and amino alkylsulfonic acid -containing organophosphonic acids，which is of very important theoretical significance and academic value for this work. It is conceived reasonablely that all the organophosphonic acids which contain the coordinating atoms such as N, S or O in their organic side chain will form organophosphonotungstic HPA of Keggin type with P:W=1:12. It is conceived reasonablely that all the organophosphonic acids which contain the coordinating atoms such as N, S or O in their organic side chain will form organophosphonotungstic HPA of Keggin type with P:W=1:12. It can be expected that more and more Keggin type organophosphonotungstic HPA with new structure, peculiar properties and specific applications would be synthesized and characterized.

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