

Synthesis and Characterization of Charge-transfer Complexes of Aminoethylphosphono- and Dimethylaminoethylphosphono-heteropolytungstic Acids of Keggin Type Structure

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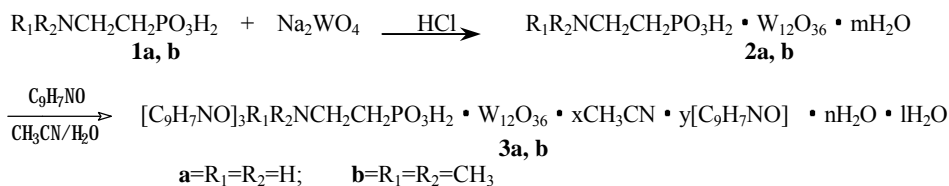
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Abstract: Two charge-transfer complexes of **2a** and **2b** of Keggin type were synthesized and characterized by elemental analysis, IR spectra, UV spectra, XRD, TG-DSC; and were compared with Hquin-PW₁₂. The primary structure of the heteropolyanions had not been changed after the formation of the charge transfer complexes.

Keywords: Aminoethylphosphonic acid, dimethylaminoethylphosphonic acid, organo-phosphono-heteropolytungstic acid, charge transfer complex, Keggin type structure.

The charge-transfer complexes of heteropoly acids (HPA) possess special properties of light, electricity and magnetism, and have attracted widespread attention by researchers in the fields of functional materials and catalysis¹. But until now, the electron acceptors of the charge-transfer complexes are the heteropolyanions with inorganic phosphoric acid, silicic acid *etc.* as the coordinate center^{2,3}, the charge-transfer complexes of Keggin type structure of the organophosphonoheteropolytungstic acids have not been reported yet.

We have synthesized HPA of the Keggin type with N-substituted β -aminoethyl-phosphonic acids as coordinate center for the first time, the research field of the Keggin type HPA was extended from inorganic phosphoric acids to organophosphonic acids⁴. In this paper, we report the synthesis and characterization of the charge-transfer complexes of organophosphonoheteropolytungstic acids of the Keggin type, **2a**, **2b** with 8-hydroxy-quinoline (Hquin). The synthetic equations are as follows:



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Experimental

C, H, N elemental analysis were performed by a PE 2400CHN instrument. IR, UV, XRD, TG and DSC were recorded on Bio-Rad FTS-185 IR spectrophotometer with KBr pellets, UV-Vis 8500 spectrophotometer, D/MAX-3C automatic X-ray diffraction instrument (Cu target) and NETZSCH STA 449C thermal-analysis instrument respectively.

Compounds **1a**, **1b** and **2a**, **2b** were prepared according to the procedure described in reference 5 and 4 respectively. Compounds **3a**, **3b** and **3c** (charge-transfer complex of **PW₁₂**) were synthesized according to the procedure described in reference 2:

2 mmol of Hquin was dissolved in 30 mL of MeCN, which was added dropwise into a solution of 0.68 mmol of **2a**, **2b** or **PW₁₂** in 50 mL of water with stirring. The mixture was refluxed at about 80°C and some yellow precipitate were formed gradually. The mixture was stand for several days at room temperature, then filtered. The yellow solid (charge-transfer complex) was kept in a desiccator containing anhydrous calcium chloride.

Results and Discussion

The characteristic IR peaks for **3a**, **3b**, **3c** and their corresponding HPA **2a**, **2b** and **PW₁₂** were given in **Table 1**. The complexes **3a**, **3b** and their corresponding HPA **2a**, **2b**, as similar as complex **3c** and its inorganic HPA **PW₁₂**, they all possess six IR characteristic peaks of heteropolyanions of Keggin type structure. The result indicated that formation of the charge-transfer complex did not change the primary structure of the heteropolyanions, but some frequency changed after the formation of the charge-transfer complexes³.

The absorption around 3450 cm⁻¹ for **3a**, **3b** and **3c** is the stretching vibration of N-H bond which were proved the formation of cation [C₉H₇ONH]⁺. Therefore, we deduced that the Hquin was protonated by **2a**, **2b**, and the charge-transfer complexes **3a**, **3b** were formed, similarly **3c** was formed from **PW₁₂**³.

Table 1 The IR data for complexes and their HPA /cm⁻¹

Sample	$\nu_{as}P-O_a$	$\nu_{as}W-O_d$	$\nu_{as}W-O_b-W$	$\nu_{as}W-O_c-W$	V	V	V/N-H
2a	1079.6*	982*	888*	799*	595*	523*	
3a	1079.5	979	896	804	596#	520	3412
2b	1080*	983*	888*	801*	595*	523*	
3b	1079.3	978	895	801.3	596#	521	3439
PW₁₂	1081	986	891	801	595	524	
3c	1080	979	896	806	596#	521	3449

multipeaks; * cited from reference 4.

The UV data for the complexes **3a**, **3b** and **3c** in MeCN and their corresponding HPA in water are given in **Table 2**. **2a**, **2b** and **PW₁₂** all have absorption peaks at 200 and 260 nm. Similar to corresponding HPA, **3a**, **3b** and **3c** all have UV absorption around 210 nm is assigned to O_d→W transfer, which was stronger, then the adsorption peaks at 262 nm which is attributed to O_{b,c}→W transfer³.

Table 2 The UV data for complexes in MeCN and heteropoly acids in water/nm

Sample	$O_d \rightarrow W$		$O_{b,c} \rightarrow W$	$W^{5+} \rightarrow W^{6+}$
3a	212	240	262	370
3b	212	240	262	
3c	206	240	262	374
2a	199*		256*	
2b	198*		256*	
PW₁₂	200*		256*	

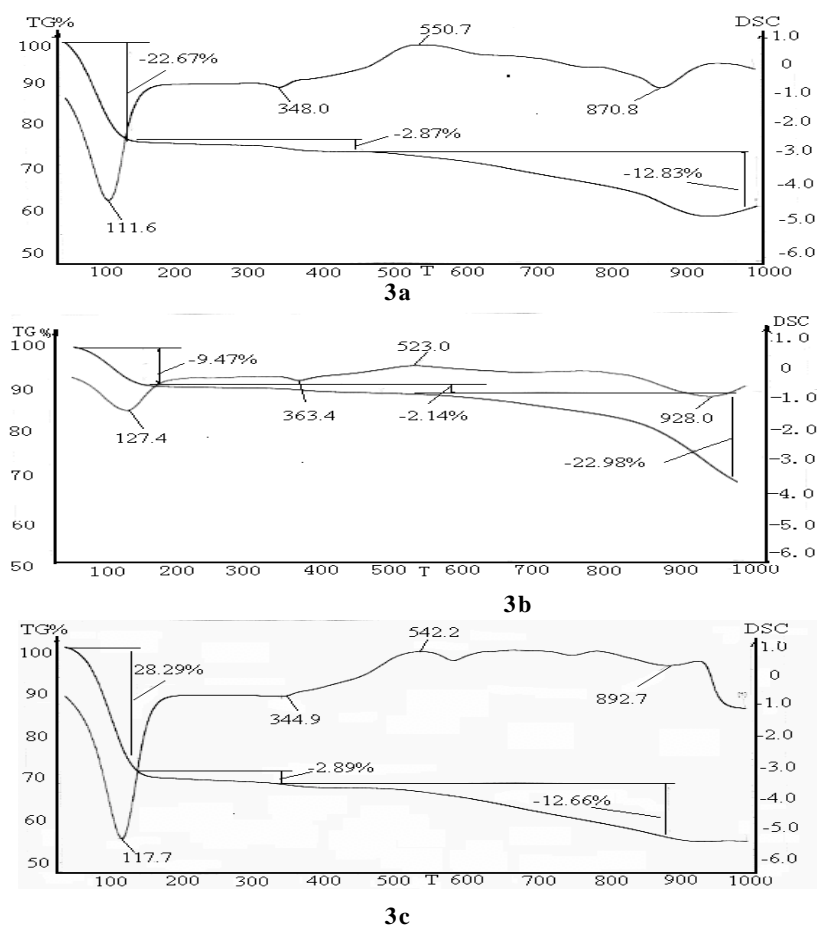
*Cited from reference 4.

Because of the heteropolyanions of complexes were reduced partially, there was an absorption peak at 370 nm caused by $W^{5+} \rightarrow W^{6+}$ transfer³, which made the energy of $O_{b,c} \rightarrow W$ transfer higher and there was an additional peak at 240 nm.

X-ray diffraction analysis for **3a**, **3b**, **3c** was shown that the characteristic peaks of Hquin and the HPA almost disappeared with some new diffraction peaks appeared. It means a new material was formed.

The thermal analysis data of **3a**, **3b** and **3c** are given in **Table 3**.

Figure 1 The TG and DSC curves for complexes **3a**, **3b**, **3c**



The TG and DSC curves for **3a**, **3b** and **3c** were similar basically. The first part of weight loss were around 30-200°C, the peaks were at 112, 127, 118°C for **3a**, **3b** and **3c** respectively. In this step, acetonitrile, adsorbed water, crystal water, adsorbed Hquin and most part of coordinate Hquin were lost. The second part of weight loss were around 200-400°C, and the peaks were at 348, 363, 345°C for **3a**, **3b** and **3c** respectively. In this step, the structural water and a small amount of Hquin were lost. The third part of weight loss were around 400-1000°C, in this step, the remaining Hquin, HPA and organophos-phonic acids decomposed⁴, the exothermic peaks were at 551, 523, 542°C.

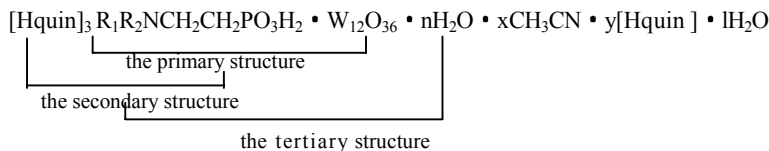
Table 3 The thermal analysis data for the complexes**3a-c**

	1st weight loss %	No. of H ₂ O lost	No. of Hquin lost	2nd weight loss %	No. of H ₂ O lost	No. of Hquin lost	3rd weight loss %	No. of Hquin lost
3a	22.67	19.12	3.57	2.87	6.03	0.04	12.83	0.39
3b	9.47	16.73	0.38	2.14	4.46	0	22.98	2.62
3c	28.29	38.13	3.51	2.89	5.97	0.13	12.66	0.86

From the data of elemental analysis and thermal analysis for **3a**, **3b** and **3c**, their compositions can be described as follows:

3a: x=1, y=1, n=9, l=16, **3b**: x=0, y=0, n=1, l=9, **3c**: x=1, y=1.5, n=16, l=28

Here x, y are the number of absorbed acetonitrile, adsorbed Hquin respectively, n is the number of crystal water and structure water, l is the number of adsorbed water which is easy to be lost even when it was kept in the desiccator. Thus, we deduced that the structure of the title compounds were as follows:



It is shown that the organophosphonoheteropolytungstic acid of the Keggin type, like the inorganic phosphotungstic acid, can form charge-transfer complex with organic substrate, retaining the primary structure of the heteropolyanion of the Keggin type in the complex. It is of very important theoretical and actual significance of this work, which will help to extend the field of catalysts, functional materials and improve their properties.

Acknowledgment

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References

1. M. T. Pope, A. Muller, *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers, Netherlands, **1994**, P245.
2. D. Attanasio, M. Bonamico, V. Fares, *J. Chem. Soc. Dalton Trans.*, **1990**, 3221.
3. S. Z. Liu, Z. J. Ku, Z. Wang, J. Y. Chen, *J. Inorg. Chem.*, **1999**, 15 (2), 263.
4. X. K. Fu, J. R. Chen, L. Q. Li, X. B. Ma, *Science in China*, **2001**, 31 (4), 349.
5. X. K. Fu, C. B. Gong, X. B. Ma, S. Y. Wen, *Synth. Commun.*, **1998**, 28 (14), 2659.

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