

2.00	11.30	11.06	10.89	10.68	10.08	9.44				
	4.64	4.75	4.21	3.98	4.20	2.62				
	4.56	4.29	3.63	1.71	3.07	1.37				
	3.34	3.26	2.97	2.76	2.48	1.63				
3.00	10.51	10.28	10.10	9.88	9.24	8.53	7.26			
	7.89	7.65	7.90	7.24	6.55	5.80	4.37			
	7.86	7.46	7.68	6.92	6.07	5.12	3.23			
	6.55	6.32	6.44	5.86	5.16	4.35	2.79			
4.00	10.05	9.82	9.64	9.42	8.75	8.00	6.47	5.32		
	9.25	8.92	8.83	8.61	7.67	7.16	6.07	4.37		
	9.25	8.91	8.84	8.62	7.60	7.13	6.17	4.05		
	9.16	8.74	8.70	8.45	7.28	6.82	5.78	3.49		
5.00	9.75	9.51	9.33	9.11	8.43	7.66	6.13	4.79	3.60	
	9.54	9.33	9.17	8.90	8.28	7.44	5.71	4.73	3.34	
	9.55	9.41	9.28	9.03	8.49	7.66	5.82	5.43	3.91	
	10.57	10.46	10.38	9.87	9.46	8.28	5.87	6.12	3.64	
6.00	9.54	9.30	9.12	8.90	8.21	7.41	5.82	4.44	3.25	
	9.49	9.25	9.07	8.85	8.16	7.36	5.77	4.38	3.02	
	9.50	9.33	9.17	8.98	8.35	7.61	6.12	4.89	3.49	
	10.98	10.75	10.54	10.33	9.61	8.74	7.04	5.55	3.43	
7.00	9.38	9.14	8.96	8.74	8.04	7.23	5.60	4.17	2.99	
	9.37	9.13	8.95	8.73	8.03	7.22	5.59	4.17	2.99	
	9.38	9.19	9.04	8.83	8.19	7.43	5.91	4.65	3.69	
	10.84	10.59	10.50	10.21	9.38	6.68	7.24	6.08	4.69	
10.00	9.08	8.84	8.66	8.44	7.73	6.89	5.18	3.70	2.53	0.19
	9.08	8.84	8.66	8.44	7.73	6.89	5.18	3.70	2.53	0.19
	9.09	8.88	8.71	8.49	7.81	7.00	5.34	3.93	2.87	0.73
	9.83	9.62	9.41	9.20	8.49	7.66	6.00	4.53	3.47	1.38
50.00	8.47	8.23	8.05	7.82	7.09	6.20	4.34	2.77	1.64	0.07
	8.47	8.23	8.05	7.82	7.09	6.20	4.34	2.77	1.64	0.07
	8.47	8.23	8.05	7.82	7.09	6.21	4.35	2.78	1.66	0.08
	8.49	8.24	8.08	7.82	7.10	6.23	4.36	2.79	1.67	0.08

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## Reactions of Oxomolybdenum(V) with the 17-tungsto-2-phosphate Anion

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Reactions of  $\text{MoOCl}_5^{2-}$  with  $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  have been studied spectrophotometrically and several complexes have been identified. The transient species initially formed is probably  $[\text{Mo}_2\text{O}_4(\text{P}_2\text{W}_{17}\text{O}_{61})_2]^{18-}$ . At  $\text{pH} \leq 3$  the visible spectrum changes gradually, indicating formation of a transient isomer of  $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ , which again transforms into the stable isomer. The transient isomer absorbs light much more strongly than the stable isomer in the visible range. At  $\text{pH} > 3$   $[\text{P}_2\text{W}^{\text{V}}\text{W}_{16}\text{O}_{61}]^{11-}$  is formed probably via the transient isomer of  $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{61}]^{7-}$ .

## Introduction

Recently we have investigated reactions of  $\text{MoO}_3^{3+}$  with

$[\text{PW}_{11}\text{O}_{39}]^{7-}$  and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  spectrophotometrically and found several transient complexes.<sup>1</sup> Now we have extended this work to the reaction of  $\text{MoO}_3^{3+}$  with  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ ,

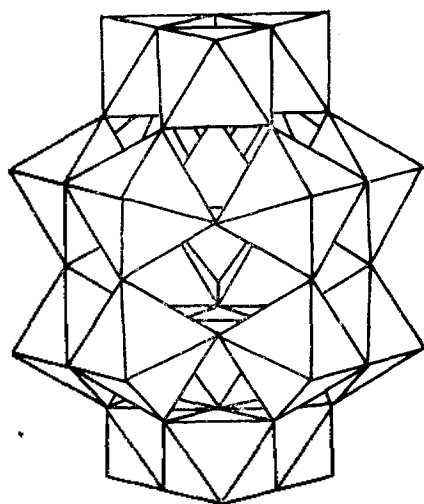
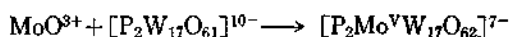


Figure 1. A polyhedron model of  $\alpha$ - $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  (Dawson structure).

#### a lacunary Dawson anion.<sup>2</sup>

A polyhedron model of the Dawson structure is shown in Figure 1. When a  $\text{WO}_4^{4-}$  group is removed from this structure, a lacunary anion  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  is formed. Depending upon the site from which the  $\text{WO}_4^{4-}$  group is removed, two different isomers are formed, one having a lacuna in the equatorial site ( $\alpha_1$ -isomer) and the other having a lacuna in the polar site ( $\alpha_2$ -isomer). In solution  $\alpha_1$ -isomer is known to change to the more stable  $\alpha_2$ -isomer.<sup>2</sup> Thus, when a solution of  $\text{VOSO}_4$  was treated with  $\alpha_1$ -isomer, a mixture of  $\alpha_1$ - $[\text{P}_2\text{VW}_{17}\text{O}_{62}]^{8-}$  and  $\alpha_2$ - $[\text{P}_2\text{VW}_{17}\text{O}_{62}]^{8-}$  was obtained.<sup>3</sup>

Since we were interested in observing transient complexes that might be formed during the reaction between  $\text{MoO}^{3+}$  and  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ , we used the more stable  $\alpha_2$ -isomer. When these species react, formation of  $\alpha_2$ - $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$  is expected.



The product may also be prepared by the reduction of  $[\text{P}_2\text{Mo}^{\text{VI}}\text{W}_{17}\text{O}_{62}]^{6-}$ , the synthesis and polarogram of which were reported recently.<sup>4</sup>

In this paper we report some properties of several complexes that are formed by the reaction of  $\text{MoO}^{3+}$  with  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ .

#### Experimental Section

**Preparation of Compounds.**  $\text{K}_6[\text{P}_2\text{W}_{18}\text{O}_{62}] \cdot n\text{H}_2\text{O}$  and  $\alpha_2$ - $\text{K}_{10}[\text{P}_2\text{W}_{17}\text{O}_{61}] \cdot 7\text{H}_2\text{O}$  were prepared according to the methods of Souchay.<sup>5</sup>  $\alpha_2$ - $\text{K}_6[\text{P}_2\text{MoW}_{17}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$  and  $(\text{NH}_4)_2[\text{MoOCl}_5]$  were prepared according to the methods of Contant<sup>4</sup> and Saha<sup>6</sup>, respectively.

A solution containing the reduced anion  $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$  was obtained by reaction of mercury with  $[\text{P}_2\text{Mo}^{\text{VI}}\text{W}_{17}\text{O}_{62}]^{6-}$  in 1N HCl solution. When the solution was filtered, and solid KCl was added to the filtrate, a black precipitate was formed immediately. The infrared spectrum of this precipitate, believed to be the potassium salt of  $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ , is shown in Figure 4.

Equal moles of  $\text{K}_{10}[\text{P}_2\text{W}_{17}\text{O}_{61}]$  and  $(\text{NH}_4)_2\text{MoOCl}_5$

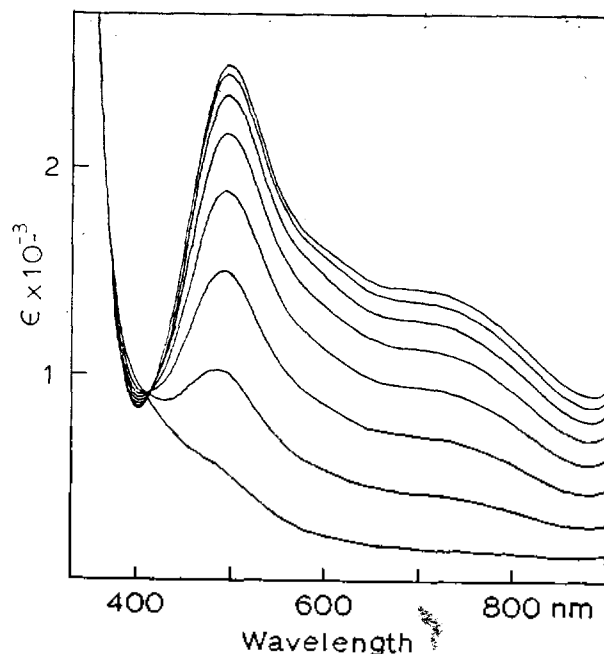


Figure 2. The development of Spectrum A in the  $[\text{MoOCl}_5]^{2-}$ - $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  system ( $\text{pH}=2.1$ ).

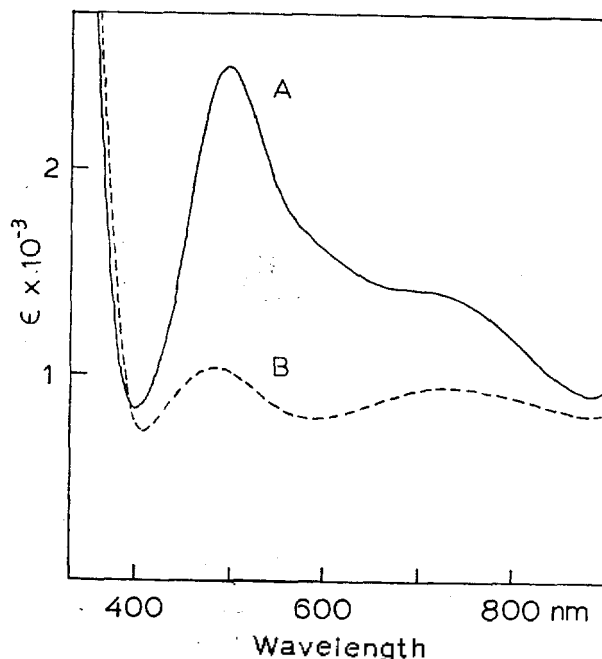
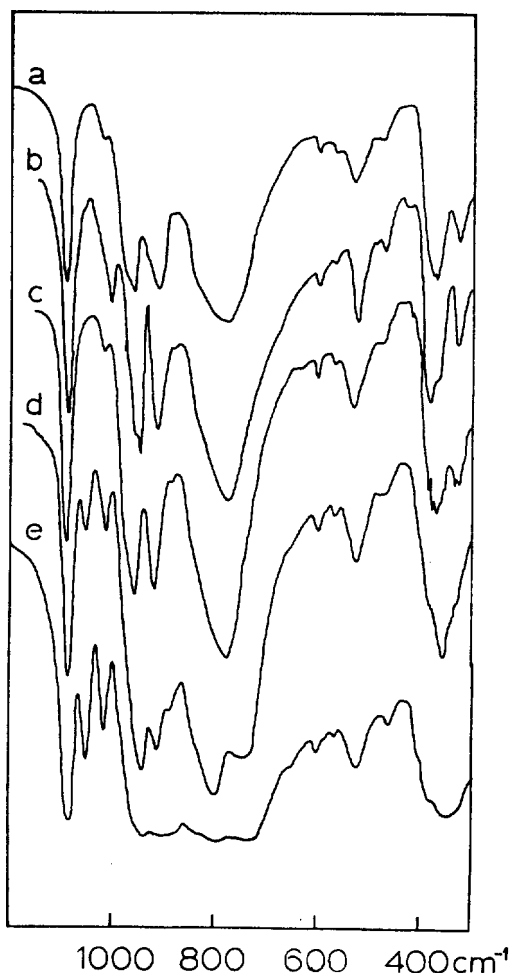


Figure 3. Spectra A and B in the  $[\text{MoOCl}_5]^{2-}$ - $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  system ( $\text{pH}=2.1$ ). See the text.

were dissolved in 0.01N HCl and the absorbance at 494 nm was observed. When the absorbance reached the maximum, a saturated solution of tetraethylammonium chloride was added to the solution. A purple precipitate was formed immediately; however, the color of the precipitate changed to black on drying. The infrared spectrum of the black precipitate was recorded.

Equal moles of  $\text{K}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$  and  $(\text{NH}_4)_2\text{MoOCl}_5$  were dissolved in an acetate buffer of pH 6.7. When the blue color developed completely, solid KCl was added to the solution. A blue precipitate was formed. The infrared spectrum of this



**Figure 4.** Infrared spectra of (a)  $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ , (b) the black precipitate, initially purple (isolated at pH 2), (c)  $\alpha_2\text{-}[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ , (d)  $[\text{P}_2\text{W}^{\text{V}}\text{W}_{16}\text{O}_{61}]^{11-}$  (isolated at pH 6.7), and (e)  $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ .

precipitate, believed to be the potassium salt of  $[\text{PW}^{\text{V}}\text{W}_{16}\text{O}_{61}]^{11-}$ , is shown in Figure 4.

**Spectral Measurements.** Infrared and uv-visible spectra were recorded on Shimadzu IR-440 and UV-240 spectrophotometers, respectively.

## Results and Discussion

**Isomer of  $\alpha_2\text{-}[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ .** The spectral change during the reaction between  $(\text{NH}_4)_2\text{MoOCl}_5$  and  $\alpha_2\text{-K}_{10}[\text{P}_2\text{W}_{17}\text{O}_{61}]$  has been followed at pH 1–3. A typical spectral change is shown in Figure 2, where a spectrum (Spectrum A) with a peak at 494 nm (20.2 kK) and two shoulders at ca. 600 (17 kK) and 700 nm (14 kK) is seen to evolve gradually. During this period an isobestic point appeared at 408 nm. After the molar absorptivity  $\epsilon$  at 494 nm reached  $2490 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ , the spectrum changed gradually to another spectrum (Spectrum B).

Spectra A and B are quite different in shape and intensity (Figure 3). Spectrum B exhibits two bands at 476 (21.0 kK) and 740 nm (13.5 kK) and it is about half as intense as Spectrum A. The spectral data are listed below:<sup>7</sup>

Spectrum A 20.2 ( $\epsilon$  2490), 17 (sh), 14 kK (sh)

Spectrum B 21.0 ( $\epsilon$  1030), 13.5 kK ( $\epsilon$  930).

The molar absorptivity is based on the concentration of molybdenum, for we used solutions containing  $\text{Mo}:[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-} < 1$ .

Spectrum B could be obtained in another way. When a solution of  $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{6-}$  in 1N HCl was reduced by mercury, the solution exhibited Spectrum B. At higher pH (1–4.5) the rate of reduction was slow, but only Spectrum B was observed to develop gradually. Thus the species (Complex B) responsible for Spectrum B is undoubtedly  $\alpha_2\text{-}[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ .

The infrared spectrum of the potassium salt of Complex B is compared with those of  $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  and  $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  in Figure 4. It is seen that two peaks at 1090 and  $780 \text{ cm}^{-1}$  are unsplit for  $\alpha_2\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ , while they are split for  $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ . These peaks are unsplit in the spectrum of Complex B, indicating that the lacuna is filled by the molybdenum atom.

Spectrum B is similar to that<sup>8</sup> of  $[\text{PMo}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{4-}$  except that the two bands are further apart in Spectrum B. This indicates that the environments of molybdenum atoms in the two anions are not exactly the same, although they are known to occupy one of  $\text{MO}_6$  octahedra in the edge-shared  $\text{M}_3\text{O}_{13}$  group common to both structures.<sup>3</sup>

Now we will consider the species responsible for Spectrum A. The spectral change indicates that a transient species (Complex A) is formed first and then it is converted gradually to Complex B. Thus both complexes are expected to contribute to Spectrum A. This explains why the maximum observable intensity of Spectrum A was dependent upon pH.

The maximum molar absorptivity at 20.2 kK that we measured for Spectrum A was  $2490 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$  at pH 2.1. This means that the molar absorptivity of Complex A at 20.2 kK is greater than  $2490 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ , since Complex A absorbs light most strongly in the visible range among the molybdenum complexes which contribute to Spectrum A.<sup>9</sup> Such a strong absorption in the visible range must be the intervalence charge transfer spectrum due to  $\text{Mo}(\text{V}) \rightarrow \text{W}(\text{VI})$  transitions.<sup>10</sup> Therefore Complex A is undoubtedly an  $\text{Mo}-[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  complex.

We have tried to precipitate out a salt of Complex A, when the absorbance at 20.2 kK reached the maximum value. Adding potassium chloride did not cause precipitation in contrast to Complex B whose potassium salt is easily precipitated out. But a purple precipitate was formed immediately when tetraethylammonium chloride was added. However, the color of the precipitate changed to black on drying. The infrared spectrum of the black precipitate agreed with that of Complex B as shown in Figure 4. These results suggest that Complex A (the purple precipitate) changes gradually to Complex B even in the solid state.

On the basis of these observations, we assume that the molybdenum atom in Complex A is halfway inside the lacuna. Then, the lacuna probably changes its form slightly to accommodate the molybdenum atom snugly. This adjustment

of the lacuna corresponds to the transformation of Complex A into Complex B.

**Complex of  $\text{Mo}_2\text{O}_4^{2+}$  with  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ .** The appearance of an isosbestic point in Figure 2 indicates formation of another transient complex. When  $(\text{NH}_4)_2\text{MoOCl}_5$  is dissolved in an acidic solution, molybdenum exists mostly in the form<sup>11</sup> of  $\text{Mo}_2\text{O}_4^{2+}$ .  $\text{Mo}_2\text{O}_4^{2+}$  has six coordination sites and forms complexes with various ligands. Recently we have reported  $[\text{Mo}_2\text{O}_4(\text{P}_3\text{O}_{10})_2\text{H}_n]^{n-8}$ , where two  $\text{P}_3\text{O}_{10}^{5-}$  anions coordinate to  $\text{Mo}_2\text{O}_4^{2+}$  as tridentate ligands,<sup>12</sup> and proposed<sup>1</sup> that  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  ligate to  $\text{Mo}_2\text{O}_4^{2+}$  as tridentate ligands, forming  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$  and  $[\text{Mo}_2\text{O}_4(\text{SiW}_{11}\text{O}_{39})]^{14-}$ . Here we propose that a similar complex  $[\text{Mo}_2\text{O}_4(\text{P}_2\text{W}_{17}\text{O}_{61})_2]^{18-}$  is formed. The molar absorptivity of this complex at the isosbestic point (408 nm) is  $890 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ . This absorption is about ten times as intense as that of  $\text{Mo}_2\text{O}_4^{2+}$  at pH 2. Such an enhancement of spectral intensity was observed<sup>1,13</sup> upon complexation of  $\text{Mo}_2\text{O}_4^{2+}$  with  $\text{P}_2\text{O}_7^{4-}$ ,  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ , or  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ .

In an earlier paper<sup>1</sup> we argued that  $[\text{PMo}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{4-}$  is not formed directly from  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$ , but by the reaction of  $\text{MoO}^{3+}$  with  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ . We assume that  $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$  is also formed by the reaction of  $\text{MoO}^{3+}$  with  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ .

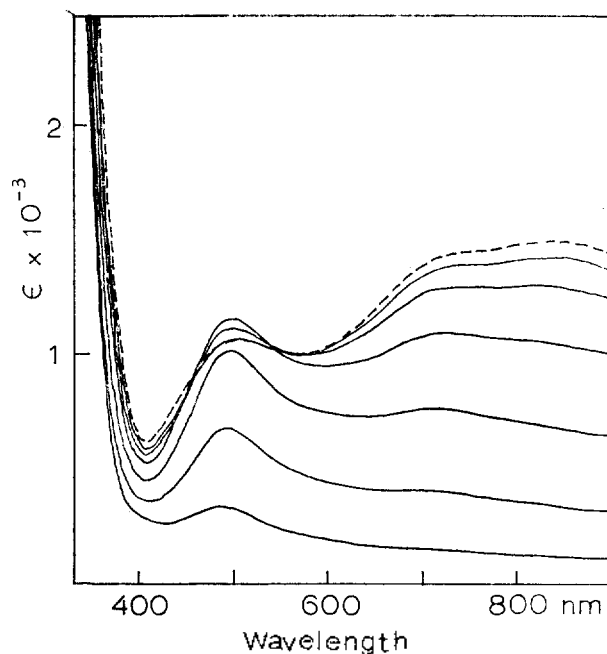
**Reactions at Higher pH.** We have observed formation of another species at higher pH. When 0.45 ml of  $9.78 \times 10^{-3} \text{ M}$   $(\text{NH}_4)_2\text{MoOCl}_5$  in water was added to 5.0 ml of  $0.906 \times 10^{-3} \text{ M}$   $\alpha\text{-K}_{10}[\text{P}_2\text{W}_{17}\text{O}_{61}]$  in an acetate buffer of pH 4.5, the spectral change was as shown in Figure 5. The initially developed spectrum appears to be Spectrum A, but it changes gradually to another spectrum where the long-wave region (700–900 nm) is more intense than the 496 nm band. This indicates that a third species (Complex C) is formed at higher pH. On examining the pH dependence of the spectra, we have found that the relative intensity of the long-wave region increases as the pH of the solution is raised, indicating that the spectrum is a composite one.

In order to identify Complex C we investigated a still higher pH region. When an aqueous solution of  $(\text{NH}_4)_2\text{MoOCl}_5$  was added to  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  in an acetate buffer of pH 6.7, blue color did not develop. However, when  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  was replaced by  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ , the spectrum (Spectrum C) shown in Figure 6 developed gradually. This spectrum changes to a slightly different spectrum (Spectrum C') in one day. Spectrum C is quite different from a spectrum where the Mo(V)→W(VI) intervalence charge transfer transition is the main feature, but very similar to that<sup>14</sup> of  $[\text{P}_2\text{W}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ ; see Figure 6.

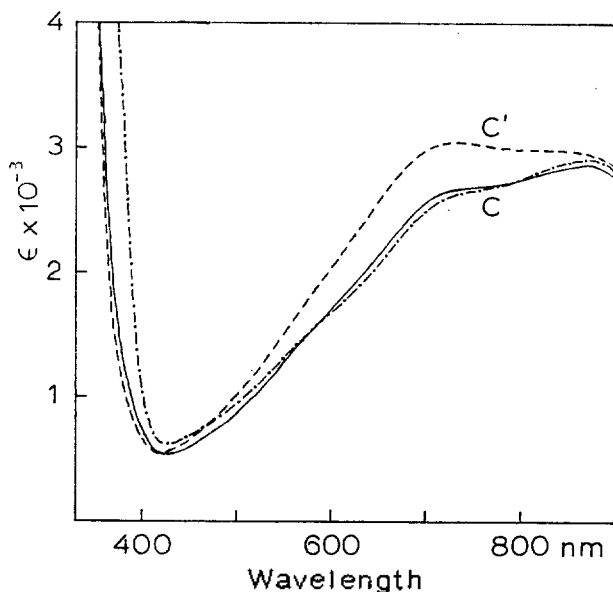
The visible spectrum of the potassium salt isolated at pH 6.7 was the same as Spectrum C at pH 2, while it was similar to Spectrum C' at pH 6.7. This indicates that the salt contains Complex C' (the species responsible for Spectrum C'), which is rapidly converted into Complex C at pH 2.

The infrared spectrum of the potassium salt is shown in Figure 4. It is seen that the spectrum is similar to that of  $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ , which has a lacuna in a polar site.

Considered together, the spectroscopic evidence indicates



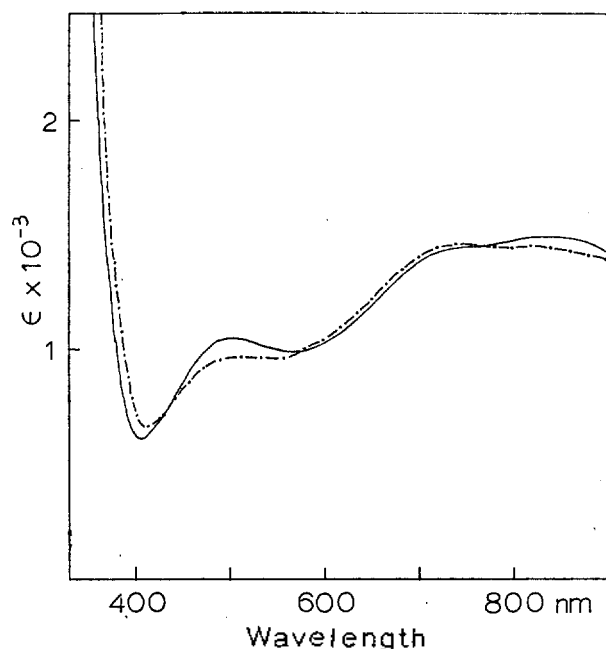
**Figure 5.** The development of a composite spectrum at pH 4.5. The dashed line represents the final spectrum.



**Figure 6.** Spectra C (—) and C' (---) observed in the  $[\text{MoOCl}_5]^{2-}\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  system (pH=6.7). -.-.- represents the spectrum of  $[\text{P}_2\text{W}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$  in 1N HCl, its intensity being 65 % of the reported value.

that Complex C' is a lacunary anion where the electron is trapped in a tungsten atom, *viz.*,  $\alpha_2\text{-}[\text{P}_2\text{W}^{\text{V}}\text{W}_{16}\text{O}_{61}]^{11-}$ . Since the equatorial tungsten atom is more easily reduced than the polar tungsten atom,<sup>15</sup> the visible spectrum of this anion is expected to be similar to that of  $[\text{P}_2\text{W}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ , as was observed in this work.

The question arises as to how  $\alpha_2\text{-}[\text{P}_2\text{W}^{\text{V}}\text{W}_{16}\text{O}_{61}]^{11-}$  is formed by the reaction of  $\text{MoO}^{3+}$  with  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ . We propose the following mechanism. At pH 6.7  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  decomposes into  $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  and tungstates<sup>14,16</sup>.



**Figure 7.** The composite spectrum (—) at pH 4.5 and the calculated spectrum (---) by mixing 70% Spectrum B and 30% Spectrum C.

Then  $\alpha_2-[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  reacts with  $\text{MoO}_3^{3+}$  to form Complex A as at lower pH, but this complex is not observed spectrophotometrically since electron is transferred rapidly from the molybdenum atom to one of the equatorial tungsten atoms. Finally the molybdenum atom which has been halfway inside the lacuna is removed after the electron transfer. Complex C thus formed is converted slowly into the more stable Complex C', which is probably an isomer of Complex C.

At pH 4.5 Complex A can be converted into either Complex B or Complex C. Thus the spectrum we observed (Figure 5) must be a composite spectrum of Spectra B and C; in fact, it could be reasonably simulated by mixing 70% of Spectrum B and 30% of Spectrum C. See Figure 7.

#### Concluding Remarks

In this work we have discovered the transient purple complex, which changes into the stable complex  $[\text{P}_2\text{Mo}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{8-}$  at low pH and  $[\text{P}_2\text{W}^{\text{V}}\text{W}_{16}\text{O}_{61}]^{11-}$  at high pH. Probably the latter reaction is the first case, in which W (VI) is reduced by Mo (V). Further work is needed to establish the structural characteristic of the purple species.

It will be worthwhile to measure the infrared spectrum of this species before it is converted to the black species. We hope that studies on the transient species shed light on the relationship between the structure of heteropoly blues and the intervalence charge transfer bands.<sup>17,18</sup>

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