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## Heteropoly Blues. IV. Spectroscopic and Magnetic Properties of Some Reduced Polytungstates<sup>1</sup>

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Optical, electron spin resonance, and nuclear magnetic resonance spectra of aqueous solutions of one- and two-electron blues derived from eight 1:12- and 2:18-heteropolytungstates have been measured. ESR  $g$  values for the one-electron blues are characteristic of tetragonal W(V) complexes. No hyperfine structure ( $^{183}\text{W}$ ,  $I = 1/2$ ) was observed due to the broadness of the signals (100–200 G at 77°). According to nmr and esr the two-electron blues are spin-paired at 77 and 310°K. The optical spectra of the reduced species show broad mixed-valence bands at 8–20 kK. The one- and two-electron heteropoly blues are regarded as class II mixed-valence species with trapped tungsten(V) valences and with intraionic electron transfer occurring at a rate which is slow on the esr time scale ( $\approx 10^8 \text{ sec}^{-1}$ ). Reduction of  $\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}^{6-}$  and  $\text{Fe}^{\text{II}}\text{W}_{12}\text{O}_{40}^{6-}$  leads to heteropoly blues containing Co(II) and Fe(III) central atoms which are effectively electronically isolated from the reduced tungstate networks.

### Introduction

The electrochemical behavior of several 1:12- and 2:18-heteropolytungstates has been described in the earlier papers of this series.<sup>3–5</sup> Much similar work has been reported by Souchay and his colleagues,<sup>6</sup> with perhaps more emphasis on the analogous molybdates. In order to examine further the electronic structures of the reduced heteropolytungstates, we have prepared solutions of the one- and two-electron blues<sup>7</sup> by controlled-potential electrolysis and measured the magnetic and optical spectra of these solutions. Since this work was started, two other esr studies of reduced heteropolyanions have been reported.<sup>8,9</sup>

### Experimental Section

**Preparation of Compounds.**—The preparations and analyses of sodium, potassium, or ammonium salts of the 1:12- and 2:18-heteropolytungstates have been described previously.<sup>3,4</sup> Generation of solutions containing the appropriate reduced species was accomplished by controlled-potential electrolysis on a mercury-pool cathode, using either manual control or a McKee-Pederson Model MP-1026 voltage source operated automatically as a potentiostat. The appropriate potentials for reduction were determined from polarograms,<sup>3,4</sup> and concentrations of the heteropolyanions ranged from  $10^{-4}$  to  $5 \times 10^{-2} M$ . The extent of reduction was determined polarographically. The reduced solutions were transferred to spectroscopic cells, etc., using hypodermic syringes equipped with platinum needles since stainless steel reduces some of the anions in acidic solution.

**Optical Spectra.**—Absorption spectra were recorded on Cary 14 and 15 spectrophotometers using 1.00-, 0.10-, and 0.05-cm quartz cells. For the reduced solutions the cells were fitted with serum caps and thoroughly flushed with purified nitrogen before use. The absorbances of the reduced solutions were routinely moni-

tored at the wavelengths of maximum absorption for 1 hr to check that no oxidation was occurring.

**Electron Spin Resonance.**—Unless otherwise stated, all measurements were made on frozen solutions at 77°K contained in 3-mm quartz tubes. A Varian V-4500 spectrometer was used. To determine the  $g$  values, the magnetic field was measured by an Alpha Scientific Laboratories nmr probe, and the microwave frequency was measured by a Mornay-Bonardi cavity wave-meter.

**Magnetic Susceptibility and Nmr Measurements.**—Probe-temperature ( $37.0 \pm 0.5^\circ$ ) susceptibilities of reduced solutions were determined by nmr techniques using a Varian A-60 spectrometer. The static method of Reilly, *et al.*,<sup>10</sup> was used predominantly, although in a few cases the results were checked using the spinning method of Evans.<sup>11</sup> Spectral grade cyclohexane was used as the reference liquid in the static method and water was used in the spinning method. Diamagnetic corrections were determined from measurements made on solutions of the oxidized anions. Paramagnetic standards used were  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ . Using published data,<sup>12,13</sup> the molar susceptibilities of these substances were evaluated to be  $(1440 \pm 30) \times 10^{-6}$  and  $(2160 \pm 70) \times 10^{-6}$  cgsu, respectively, at 37°. Chemical shifts of nmr spectra are reported with reference to an internal standard of Tiers' salt [sodium 3-(trimethylsilyl)-1-propanesulfonate].

TABLE I  
UV SPECTRAL DATA FOR OXIDIZED  
HETEROPOLYTUNGSTATES IN 1.0 M SULFURIC ACID

Anion	Position of max, kK	Anion	Position of max, kK
$\text{PW}_{12}\text{O}_{40}^{3-}$	37.74 (3) <sup>a</sup>	$\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$	38.83 (3) <sup>b</sup>
$\text{SiW}_{12}\text{O}_{40}^{4-}$	38.17 (3)	$A\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$	34.0, <sup>c</sup> 39.22 (5)
$\text{FeW}_{12}\text{O}_{40}^{5-}$	37.88 (3) <sup>b</sup>	$B\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$	34.2, <sup>c</sup> 40.8 <sup>c</sup>
$\text{CoW}_{12}\text{O}_{40}^{6-}$	38.31 (3) <sup>b</sup>		

<sup>a</sup> Uncertainty in terms of last figure. <sup>b</sup> Also observed in water solution at pH 6. <sup>c</sup> Shoulder.

### Results

**Optical Spectra.**—The oxidized 12-tungstates exhibit a characteristic intense absorption band ( $\epsilon_{\text{max}} \text{ ca. } 5 \times$

(1) This series of papers is based in part on the Ph.D. theses of G. M. V. (1967) and E. P. (1968), Georgetown University.

(2) Author to whom correspondence should be addressed.

(3) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).

(4) M. T. Pope and E. Papaconstantinou, *ibid.*, **6**, 1147 (1967).

(5) E. Papaconstantinou and M. T. Pope, *ibid.*, **6**, 1152 (1967).

(6) For a recent review of this work see R. Massart and G. Hervé, *Rev. Chim. Mineral.*, **5**, 501 (1968).

(7) In the absence of an approved system of nomenclature, the reduced heteropolyanions are referred to as  $n$ -electron blues. Thus the one-electron blue of 12-tungstophosphate is  $[\text{PW}_{12}\text{O}_{40}]^{4-}$ , etc.

(8) P. Rabette, C. Ropars, and J.-P. Grivet, *Compt. Rend.*, **C265**, 153 (1967).

(9) P. Stonehart, J. G. Koren, and J. S. Brinen, *Anal. Chim. Acta*, **40**, 65 (1968).

(10) C. A. Reilly, H. M. McConnell, and R. G. Meisenheimer, *Phys. Rev.*, **98**, 264A (1955); J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957); D. C. Douglass and A. Fratiello, *J. Chem. Phys.*, **39**, 3161 (1963); H. A. Lauwers and G. P. Van der Kelen, *Bull. Soc. Chim. Belges*, **75**, 238 (1966).

(11) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(12) W. J. de Haas and C. J. Gorter, *Koninkl. Ned. Akad. Wetenschap., Proc., Ser. B*, **33**, 1101 (1930); R. J. Benzie and A. H. Cooke, *Proc. Phys. Soc. (London)*, **A64**, 124 (1951).

(13) H. C. Clark, N. F. Curtis, and A. L. Odell, *J. Chem. Soc.*, 63 (1954).

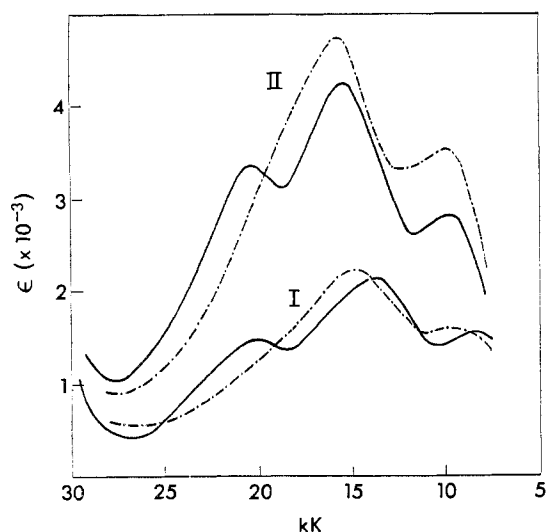


Figure 1.—Representative absorption spectra of heteropoly blues in the visible-ir region: I, one-electron blues; II, two-electron blues of 12-tungstophosphate (—) and 12-tungstocobaltate(II) (---).

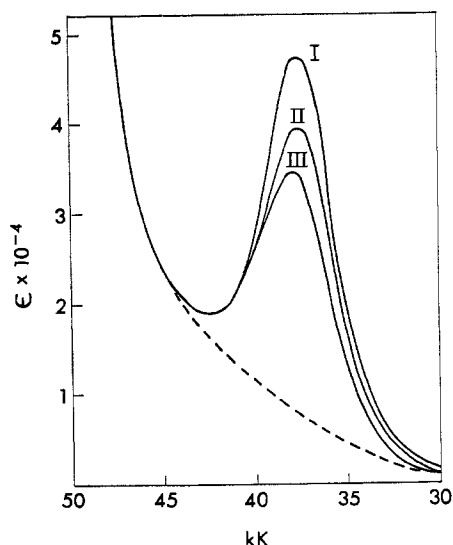


Figure 2.—Variation in intensity of the 38-kK band of 12-tungstophosphate upon reduction: I, oxidized anion; II, one-electron blue; III, two-electron blue. (Solvent, 1.0 *M* sulfuric acid.)

TABLE II  
VISIBLE-INFRARED ABSORPTION SPECTRAL MAXIMA OF HETEROPOLY BLUES

Anion	Solvent	Band I <sup>a</sup>	Band II <sup>b</sup>	Band III <sup>a</sup>
PW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	1.0 <i>M</i> H <sub>2</sub> SO <sub>4</sub>	8.0 (1600 <sup>c</sup> )	13.3 (2000)	20.5 (1200)
PW <sub>12</sub> O <sub>40</sub> <sup>5-</sup>	1.0 <i>M</i> H <sub>2</sub> SO <sub>4</sub>	9.0 (3000)	15.3 (4400)	20.4 (3300)
SiW <sub>12</sub> O <sub>40</sub> <sup>5-</sup>	1.0 <i>M</i> H <sub>2</sub> SO <sub>4</sub>	8.6 (1500)	13.7 (2100)	20.0 (1200)
SiW <sub>12</sub> O <sub>40</sub> <sup>6-</sup>	1.0 <i>M</i> H <sub>2</sub> SO <sub>4</sub>	10.0 (2800)	16.0 (3800)	20.0 (2800)
FeW <sub>12</sub> O <sub>40</sub> <sup>6-</sup>	pH 6.6 <sup>d</sup>	8.5 (1300)	14.0 (2800)	Ca. 20 sh <sup>e</sup> (900)
FeW <sub>12</sub> O <sub>40</sub> <sup>7-</sup>	pH 6.6 <sup>d</sup>	9.5 (3100)	15.8 (4100)	Ca. 20 sh (3000)
CoW <sub>12</sub> O <sub>40</sub> <sup>7-</sup>	pH 6.6 <sup>d</sup>	Ca. 10 (1600)	15.4 (2300)	
CoW <sub>12</sub> O <sub>40</sub> <sup>8-</sup>	pH 6.6 <sup>d</sup>	Ca. 10 (3500) <sup>f</sup>	15.8 (4800) <sup>f</sup>	
H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> <sup>7-</sup>	pH 6.6 <sup>d</sup>	Ca. 8.5 (1500)	14.5 (2100)	
H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> <sup>8-</sup>	pH 6.6 <sup>d</sup>	10.0 (2800)	16.2 (3900)	
A-P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> <sup>7-</sup>	pH 1.4 <sup>g</sup>	11.2 (5400)	13.3 (6000)	
A-P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> <sup>8-</sup>	pH 1.4 <sup>g</sup>	11.3 sh (6200)	14.1 (13,100)	
B-P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> <sup>7-</sup>	pH 1.4 <sup>g</sup>	11.0 (4400)	14.0 sh (3600)	
B-P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> <sup>8-</sup>	pH 1.4 <sup>g</sup>	10.7 sh (6600)	14.4 (10,600)	

<sup>a</sup> Uncertainty  $\pm 0.5$  kK. <sup>b</sup> Uncertainty  $\pm 0.1$  kK. <sup>c</sup> Molar absorptivity  $\pm 100$  M<sup>-1</sup> cm<sup>-1</sup>. <sup>d</sup> Buffer 0.1 *M* phosphate. <sup>e</sup> Shoulder. <sup>f</sup> Spectrum identical in 1.0 *M* H<sub>2</sub>SO<sub>4</sub>. <sup>g</sup> Adjusted with H<sub>2</sub>SO<sub>4</sub>.

$10^4$  M<sup>-1</sup> cm<sup>-1</sup>) at ca. 260 nm,<sup>14</sup> and the 2:18 anions have two absorbances in this region; see Table I.<sup>15</sup>

The absorption spectra of the reduced anions show two (sometimes three) new broad bands in the visible and near-infrared regions.<sup>16</sup> The spectra are similar in form and intensity for all the 12-tungstates (see Figure 1) and are similar, but more intense, for the 2:18 species.

(14) The bands for tungstophosphate, tungstosilicate, and metatungstate have been noted by other workers [see, for example, O. Glemser, W. Holz-nagel, W. Holtje, and E. Schwartzmann, *Z. Naturforsch.*, **20b**, 725 (1965)]. D. H. Brown [*Spectrochim. Acta*, **19**, 1683 (1963)] and V. E. Simmons [Ph.D. Thesis, Boston University, 1963] first reported the uv spectra of tungstoferrate(III) and tungstocobaltate(II), respectively.

(15) The bands reported in Table I are situated on the tail of an even more intense absorption with a maximum near 50 kK. The molar absorptivity per tungsten atom at 50 kK is, for the tungstophosphates, essentially independent of the ionic structure, *i.e.*, ca. 11,000 for PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>, ca. 12,000 for A-P<sub>2</sub>W<sub>18</sub>O<sub>62</sub><sup>7-</sup>, and ca. 13,000 for B-P<sub>2</sub>W<sub>18</sub>O<sub>62</sub><sup>7-</sup>. This suggests an assignment in terms of independent W=O chromophores in these anions, *i.e.*, charge transfer from the external oxygen atoms each of which is attached to a single tungsten (see Figure 4). W. H. Nelson and R. S. Tobias [*Inorg. Chem.*, **2**, 985 (1963)] have suggested a similar assignment for the corresponding band in the spectrum of the hexatantalate anion.

(16) Published spectra for the one- and two-electron blues of tungstosilicate [P. Souchay and G. Hervé, *Compt. Rend.*, **261**, 2486 (1965)] and the one-electron blue of tungstophosphate<sup>9</sup> are in essential agreement with those reported in Table II.

Spectral data for the 14 ions studied are summarized in Table II. The ultraviolet bands (Table I) are still observed in the spectra of the reduced anions but are significantly less intense; see Figure 2. Owing to their position on the broad tail of the 50-kK absorption,<sup>15</sup> no quantitative intensity measurements were possible, except in the case of 12-tungstophosphate where an extrapolation of the tail could be made. The integrated intensity of the 38-kK band in the spectrum of PW<sub>12</sub>O<sub>40</sub><sup>5-</sup> was estimated to be  $70 \pm 5\%$  that of the corresponding band in the spectrum of the oxidized anion.

**Electron Spin Resonance.**—With the exception of the reduced tungstoferrate anion (see below), frozen solutions of the one-electron blues showed relatively broad (100–200 G) esr signals at 77°K; see Figure 3 and Table III. No hyperfine structure was observed in these spectra.

As can be seen from Figure 3, the signals for PW<sub>12</sub>O<sub>40</sub><sup>4-</sup> and SiW<sub>12</sub>O<sub>40</sub><sup>5-</sup> were anomalously weak compared with that for H<sub>2</sub>W<sub>12</sub>O<sub>40</sub><sup>7-</sup>. In general, the spec-

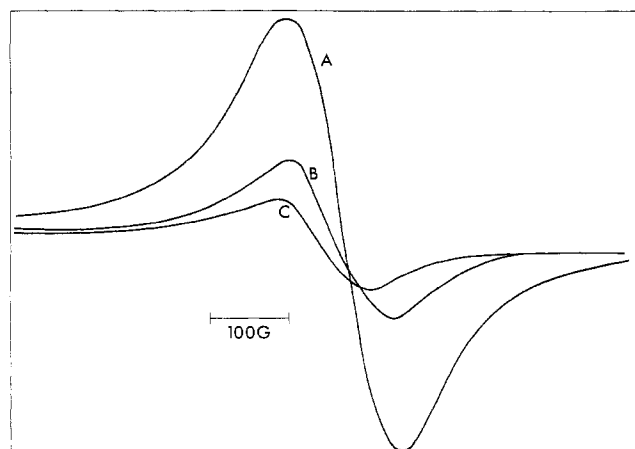


Figure 3.—Esr spectra of one-electron blues of metatungstate (A), 12-tungstosilicate (B), and 12-tungstophosphate (C) in frozen aqueous solution at 77°K. All solutions were  $1.00 \times 10^{-2} M$  in heteropolyanion and the spectrometer settings were the same for each spectrum.

tra for the 2:18 anions were more intense than those for the 12-tungstates. Thus, while the 1:12 spectra were recorded in  $10^{-3} M$  solutions at a spectrometer gain of 250, the 2:18 spectra were observed in  $2.8 \times 10^{-3} M$  solutions at a gain of 100. As the temperature was raised, the signals from the 12-tungstate blues rapidly decreased in intensity without broadening significantly and were unobservable at 130°K and above. The more intense spectra of the 2:18 anions were observable to *ca.* 230°K, the signals from  $B\text{-P}_2\text{W}_{18}\text{O}_{62}^{7-}$  and  $\text{As}_2\text{W}_{18}\text{O}_{62}^{7-}$  being isotropic above *ca.* 100°K.

TABLE III  
ESR *g* VALUES FOR HETEROPOLY BLUES IN  
FROZEN AQUEOUS SOLUTIONS AT 77°K

Anion	<i>g</i>	Anion	<i>g</i>
$\text{PW}_{12}\text{O}_{40}^{4-}$	1.826 (2) <sup>a</sup>	$A\text{-P}_2\text{W}_{18}\text{O}_{62}^{7-}$	1.852 (2)
$\text{SiW}_{12}\text{O}_{40}^{5-}$	1.819 (2)	$B\text{-P}_2\text{W}_{18}\text{O}_{62}^{7-}$	1.845, 1.852, 1.899
$\text{CoW}_{12}\text{O}_{40}^{7-}$	1.790 (5) <sup>b</sup>	$\text{As}_2\text{W}_{18}\text{O}_{62}^{7-}$ <sup>c</sup>	1.813(⊥), 1.898( )
$\text{H}_2\text{W}_{12}\text{O}_{40}^{7-}$	1.810 (2)		

<sup>a</sup> Uncertainty in terms of last figure. <sup>b</sup> Signals due to Co(II) central atom also present; see text. <sup>c</sup> See ref 25.

The spectra of  $10^{-2} M$  solutions of tungstophosphate, tungstosilicate, and metatungstate were recorded at various stages of reduction to their respective one-electron blues. While the intensities of the characteristic signals for  $\text{SiW}_{12}\text{O}_{40}^{5-}$  and  $\text{H}_2\text{W}_{12}\text{O}_{40}^{7-}$  increased continuously as the reduction proceeded, the signal intensity for the reduced tungstophosphate solution showed a maximum at 50–60% reduction and a smaller maximum at *ca.* 20% reduction. The intensity of the signal at 60% reduction was some seven times that of the 100% reduced solution. A similar experiment carried out with  $10^{-3} M$  tungstophosphate showed normal behavior up to *ca.* 50% reduction followed by no further increase in signal intensity as the reduction proceeded. At 100% reduction to  $\text{PW}_{12}\text{O}_{40}^{4-}$  the signal intensity for the  $10^{-3} M$  solution was only

slightly less than that for the fully reduced  $10^{-2} M$  solution.

During the course of reduction from the one-electron to the two-electron blue stage, solutions of tungstophosphate, tungstosilicate, and metatungstate showed esr signals steadily decreasing in intensity. No signals were observed for two-electron blues of each of the anions studied.

In the case of  $\text{CoW}_{12}\text{O}_{40}^{6-}$  and  $\text{FeW}_{12}\text{O}_{40}^{5-}$ , characteristic esr signals were observed for the paramagnetic central atoms. In 1.0 *M* sulfuric acid or 0.1 *M* phosphate buffer, pH 6.6, the spectrum of  $\text{CoW}_{12}\text{O}_{40}^{6-}$  consisted of a weak asymmetric signal,  $g_{\text{eff}} = 2.19$ , and a more intense, very broad (*ca.* 900 G) asymmetric signal,  $g_{\text{eff}} = 5.2$ . The position of the weaker signal is in satisfactory agreement with the magnetic moment of  $\text{K}_5\text{H}[\text{CoW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$  determined by Simmons<sup>17</sup> ( $\mu_{\text{eff}} = 4.26 \text{ BM}$ ;  $g_{\text{eff}} = 2.20$ ). Similar *g* values have been reported for other tetrahedral Co(II) species.<sup>18</sup> Assignment of the  $g = 5.2$  signal is uncertain with the present data.<sup>19</sup>

Upon reduction of  $\text{CoW}_{12}\text{O}_{40}^{6-}$  to  $\text{CoW}_{12}\text{O}_{40}^{7-}$  in the pH 6.6 buffer, a third (heteropoly blue) signal,  $g = 1.790$ , appeared in the spectrum (see Table III). At the one-electron blue stage, the cobalt(II) signals were still visible although reduced in intensity. Reduction to  $\text{CoW}_{12}\text{O}_{40}^{8-}$  was impossible in the buffer owing to the insolubility of the two-electron blue in this medium. However, in 1.0 *M* sulfuric acid  $\text{CoW}_{12}\text{O}_{40}^{6-}$  is reduced in a single two-electron step<sup>3</sup> to  $\text{H}_2[\text{CoW}_{12}\text{O}_{40}]^{6-}$ . The esr spectrum of the two-electron blue was identical in all respects with that of the oxidized anion.

Solutions ( $10^{-4}$  to  $10^{-2} M$ ) of tungstoferrate(III) in neutral solvents (pH 6.6 buffer, 1.0 *M* and saturated sodium sulfate) gave an intense symmetrical signal some 250 G wide,  $g = 1.997 \pm 0.002$ , close to the spin-only value expected for a tetrahedral Fe(III) species. The intensity of this signal varied as  $1/T$  in the temperature range 123–206°K. In acid solvents (sulfuric or hydrochloric acids) the signal became progressively narrower as the acidity increased. In solutions which were  $10^{-4} M$  in tungstoferrate and 1.0 *M* in sulfuric acid, or  $10^{-2} M$  in tungstoferrate and 4.0 *M* in sulfuric acid, the signals were only *ca.* 30 G wide and noticeably asymmetric.<sup>20</sup>

Reduction of tungstoferrate in single-electron steps can only be carried out in neutral solutions (pH 6.6).<sup>3</sup> At the one-electron stage no characteristic "heteropoly blue" esr signal was observed, and the relaxation time of the Fe(III) had decreased so much that its signal was barely detectable. As reduction continued, the Fe(III) signal gradually reappeared, and at the two-electron blue stage ( $\text{FeW}_{12}\text{O}_{40}^{7-}$ ) it had regained its

(17) V. E. Simmons, Ph.D. Thesis, Boston University, 1963.

(18) E. König, "Magnetic Properties of Coordination and Organometallic Transition Metal Compounds," in Landolt-Börnstein, "Zahlenwerte und Funktionen," New Series, Vol. II/2, K. H. Hellwege and A. M. Hellwege, Ed., Springer-Verlag, Berlin, and New York, 1966.

(19) The signal may be due to the  $1/2 \rightarrow 3/2$  transition. Further single-crystal work is planned in order to assess more accurately the magnitude of the zero-field splitting in this complex.

(20) The signals were not sufficiently asymmetric to show perpendicular and parallel components.

characteristic shape and width, although it was only about one-third the original intensity.

**Magnetic Susceptibilities.**—According to both static and spinning methods, the paramagnetic susceptibility of reduced tungstophosphate solutions ( $5.0 \times 10^{-2}$  and  $2.0 \times 10^{-2} M$  in  $1.0 M H_2SO_4$ ) increased steadily to a maximum ( $(800 \pm 100) \times 10^{-6}$  cgsu) at the one-electron stage and then decreased steadily to zero for solutions containing the two-electron blue. Similar behavior was observed for reduced solutions of tungstosilicate in  $1.0 M$  sulfuric acid. The effective magnetic moments (BM) for the one-electron blues were:  $PW_{12}O_{40}^{4-}$ ,  $1.4 \pm 0.1$ ;  $SiW_{12}O_{40}^{5-}$ ,  $1.3 \pm 0.1$ ;  $H_2W_{12}O_{40}^{7-}$ ,  $1.4 \pm 0.1$ , the last being measured in pH 6.6 buffer.

**Nuclear Magnetic Resonance.**—Proton magnetic resonance spectra of neutral aqueous solutions containing the metatungstate anion,  $H_2W_{12}O_{40}^{6-}$ , show a narrow signal at  $\tau$  3.8 ( $\tau$  4.0 in  $1.0 M H_2SO_4$ ) which has been identified with the two hydrogen atoms occupying the central tetrahedral cavity of the Keggin structure.<sup>21</sup> Upon reduction of  $0.1 M$  sodium metatungstate in a pH 6.6 buffer, the  $\tau$  3.8 signal rapidly broadened and was eventually unobservable but returned to its normal shape when the solution was allowed to reoxidize. When the metatungstate solution was reduced completely to the two-electron blue stage, the signal reappeared, shifted slightly upfield at  $\tau$  4.5.

### Discussion

**Structural Considerations.**—The 12 tungsten atoms in a Keggin anion are structurally equivalent.<sup>22</sup> As in all other known heteropoly- and isopolyanion structures,<sup>23</sup> the addenda (tungsten) atoms are strongly displaced toward the exterior of the anion.<sup>24</sup> These atoms are therefore effectively in tetragonal oxide environments; see Figure 4. The crystal structure of the potassium salt of  $B-P_2W_{18}O_{62}^{6-}$  does not locate the oxygen atoms,<sup>25</sup> but it may be presumed that similar displacements occur in this anion. As Dawson pointed out<sup>25</sup> the  $B-P_2W_{18}O_{62}^{6-}$  structure is closely related to the Keggin structure, except that there are two kinds of tungsten atoms in the former. If the 2:18 anion is regarded as a prolate spheroid, six (Keggin-like)  $WO_6$  octahedra are situated near the poles, and twelve  $WO_6$  octahedra are equatorial. The structure of  $A-P_2W_{18}O_{62}^{6-}$  differs from that of the  $B$  isomer only in having a center of symmetry rather than an equatorial mirror plane (point group  $D_{3d}$  rather than  $D_{3h}$ ).<sup>26,27</sup>

It has been apparent for some time that the molecular

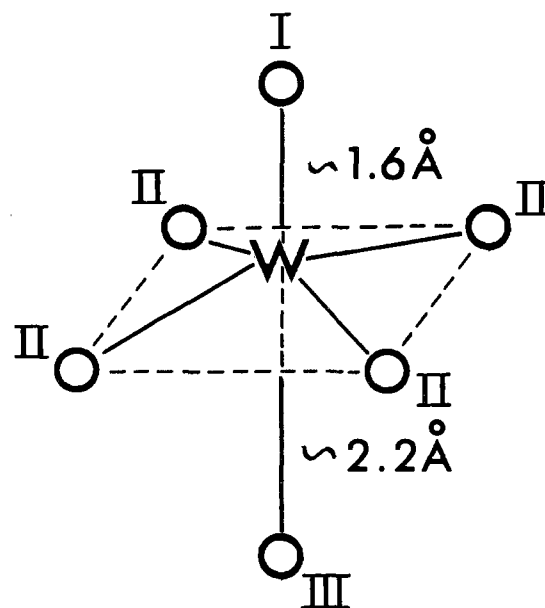


Figure 4.—Approximate environment (idealized to  $C_{4v}$  symmetry) of a tungsten atom in a 1:12 (Keggin) or 2:18 (Dawson) heteropolyanion. The bond lengths shown are based upon an incompletely refined crystal structure<sup>23</sup> and have standard deviations of  $0.2 \text{ \AA}$ . Oxygen I is on the exterior of the ion. Oxygens II participate in bridging to four neighboring tungsten atoms and in reality are not all equivalent. Oxygen III is shared by the central atom and two other tungsten atoms.

structures of heteropoly blues are essentially the same as those of the oxidized anions.<sup>28</sup> Electron<sup>29</sup> and X-ray<sup>30</sup> powder diffraction data show that the metal-oxygen framework of the Keggin structure is still present in the heteropoly blues. It can safely be assumed that no rearrangement occurs on reduction of the 2:18 anions since different esr signals were observed for the reduced isomers of  $P_2W_{18}O_{62}^{6-}$ , and no isomerization was apparent upon reoxidation.

Since it is clear both from the optical spectra (Table II) and electrochemical data<sup>3,4</sup> that the central atoms play essentially no part in the reduction of these heteropolyanions, two simple models for the electronic structures of the blues may be considered. The first model (class II according to Robin and Day's classification<sup>31</sup> of mixed-valence species) requires the "extra" electrons to be trapped on specific tungsten atoms.<sup>32</sup> In the second model (class III-A) the added electrons are completely delocalized<sup>33</sup> in a multicentered molecular orbital (*cf.* aromatic hydrocarbon radical anions and

(28) Reduction is both rapid and reversible, whereas hydrolysis of tungstates is excessively slow.

(29) I. P. Alimarin, Z. F. Shakhova, and R. K. Motorkina, *Dokl. Akad. Nauk SSSR*, **106**, 61 (1956).

(30) C. M. Tourné and P. Souchay, *Compt. Rend.*, **C263**, 1142 (1966).

(31) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 248 (1967).

(32) It is unlikely that one or two W(V) centers would be observable by X-ray diffraction techniques, since the reduced species would almost certainly crystallize with a disordered arrangement of the W(V) atoms. For example the Keggin anion with cobalt(II) replacing one of the tungstens crystallizes in this fashion: L. C. W. Baker, V. E. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, and L. L. Koh, *J. Am. Chem. Soc.*, **88**, 2320 (1966).

(33) It should be pointed out that the first model also involves delocalization of electrons, but in this case the delocalization occurs *via* a thermal (hopping) process.

(21) M. T. Pope and G. M. Varga, Jr., *Chem. Commun.*, 653 (1966).

(22) J. F. Keggin, *Proc. Roy. Soc. (London)*, **A144**, 75 (1934).

(23) A. Perloff, Ph.D. Thesis, Georgetown University, 1966; H. T. Evans, Jr., *Inorg. Chem.*, **5**, 967 (1966); H. T. Evans, Jr., *J. Am. Chem. Soc.*, **90**, 3275 (1968); D. D. Dexter and J. V. Silverton, *ibid.*, **90**, 3589 (1968).

(24) N. F. Yannoni, Ph.D. Thesis, Boston University, 1961.

(25) B. Dawson, *Acta Cryst.*, **6**, 113 (1953);  $As_2W_{18}O_{62}^{6-}$  also has the  $B$ -isomer structure according to early optical crystallography: L. Duparc and F. Pearce, *Bull. Soc. Franc. Mineral.*, **18**, 31 (1895); *Z. Krist.*, **27**, 612 (1897); **31**, 66 (1899).

(26) D. A. Langs and J. V. Silverton, in preparation.

(27) This structure ( $A$  isomer) has been illustrated: A. F. Wells, "Structural Inorganic Chemistry," 1st ed, Oxford University Press, London, 1945, p 344.

certain metal cluster complexes). We believe that the data reported here are best interpreted in terms of the first, class II, model.

**Electron Spin Resonance.**—The magnetic and esr properties of the one-electron blues are strikingly similar to those of  $\text{WOX}_5^{2-}$  complexes in which the tungsten atoms are also in tetragonal environments. The  $g$  values reported in Table III may be compared with those of  $\text{WOBr}_5^{2-}$  [1.940 ( $\parallel$ ), 1.775 ( $\perp$ )<sup>34</sup>] for example. In general, esr line widths for  $\text{WOX}_5^{2-}$  complexes are broader than those for the corresponding  $\text{MoOX}_5^{2-}$  species because of the increased effect of spin-orbit coupling upon the (spin-lattice) relaxation times of the tungsten complexes. Thus, for example, Kon and Sharpless<sup>34</sup> were unable to observe hyperfine structure (hfs) due to  $^{183}\text{W}$  ( $I = 1/2$ , 14.28%) in the spectrum of  $\text{WOCl}_5^{2-}$  at room temperature because of excessive line width ( $\Delta H_{\text{max slope}}$  ca. 100 G) although  $^{93,95}\text{Mo}$  hfs was clearly visible in the spectrum of  $\text{MoOCl}_5^{2-}$  under the same conditions, in spite of a less favorable hyperfine coupling tensor for this complex. Since the line widths of the heteropoly blue spectra ranged from 100 to 200 G, it is not surprising that hfs was undetected.<sup>35</sup> The signals are unusually broad even for tungsten(V) species, and there is a strong temperature dependence of line width, indicating an efficient mechanism for spin relaxation in the heteropoly blues which is not present in the mononuclear W(V) complexes. Such a mechanism could be provided by rapid intraionic electron transfer.<sup>36</sup> In this connection we may note that the relaxation times are detectably longer in the reduced 2:18 anions (narrower lines, anisotropic signals at 77°K) which would indicate firmer trapping of the electrons in these species. This may mean that it is the "equatorial" (non-Keggin-like) tungsten atoms which are reduced first in the 2:18 anions.

We are, at present, unable to offer a completely satisfactory explanation for the variation in esr signal intensity as solutions of tungstophosphate are reduced. Somewhat similar behavior has been noted by Stonehart and coworkers<sup>9</sup> in the reduction of solutions of sodium tungstate in phosphoric acid.<sup>37</sup> Recent work here has shown that the one-electron blue of tungstophosphate is prone to disproportionate to the diamagnetic two-

electron blue and oxidized 11-tungstophosphate anion.<sup>38</sup> It is possible that some of the esr measurements were made on solutions which had undergone such a disproportionation.

The second electron added to these heteropolyanions clearly pairs with the first. This is shown by magnetic susceptibilities, nmr observation of the central protons in reduced metatungstate, and esr observation of Fe(III) and Co(II) in the reduced heteropolyanions. The electron pairing is probably due to superexchange rather than to the formation of a metal-metal bond. This conclusion is based on the following considerations: (1) the two-electron blue of 12-molybdosilicate *does* give an esr signal at 77°K, although the intensity is only one-third that of the one-electron blue; (2) up to the addition of four electrons, the optical spectra of isostructural molybdates and tungstates show similar changes, suggesting that their electronic structures are analogous;<sup>39</sup> (3) a pronounced distortion of the heteropolyanion structure would be expected if a metal-metal bond is formed between neighboring tungsten atoms (*cf.* W-W distances of 2.49 Å in  $\text{WO}_2$  where there is a metal-metal bond<sup>40</sup> and ca. 3.4 Å in the Keggin structure<sup>22</sup>). The isomorphism of the two-electron blue of metatungstate with the oxidized anion<sup>30</sup> suggests that no such distortion has occurred.

**Optical Spectra.**—At present, little can be said about the optical spectra of the heteropoly blues, except to note, with others,<sup>16</sup> that the extinction coefficients of the intervalence bands are roughly proportional to the number of electrons added. This factor supports the assignment of the blues as class II compounds. According to Robin and Day,<sup>31</sup> it should be possible, in a class II system, to see the crystal field spectrum of the reduced ion, shifted from where it would ordinarily appear by the energy of the lowest mixed-valence transition. Crystal field bands of W(V) in  $\text{WOCl}_5^{2-}$  occur at 14.2 and 25.2 kK.<sup>41</sup> In the heteropoly blue spectra with three bands (Table II) it will be noted that band III is separated from band I by some 12–13 kK. While this difference *may* represent the energy of the lowest d-d transition of W(V) in these complexes, such an assignment does not account for the most prominent band (II). A more probable assignment of the spectrum invokes mixed-valence transitions to different tungsten atoms. In the Keggin structure for example each  $\text{WO}_6$  octahedron is bonded to two others by mutual edge sharing and to two more by corner sharing. On the simplest model one would expect two different barriers to electron transfer.

The minor changes observed in the uv spectra upon reduction provide further confirmation of the class II nature of these particular heteropoly blues.<sup>42</sup> The 38-kK band of  $\text{PW}_{12}\text{O}_{40}^{3-}$  is still present, but at reduced

(34) H. Kon and N. E. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

(35) Rabette, *et al.*,<sup>8</sup> on the other hand were able to detect hfs in the esr spectra of some 12-molybdosilicate blues because of narrower line widths.

(36) The anomalous line shapes (broad wings) and temperature dependences of the heteropoly blue spectra may be rationalized in the following manner. The line widths are governed primarily by two relaxation times, the first (spin-lattice) increases as the temperature is lowered, and the second (affected by the lifetime of an electron on a particular tungsten) increases as the temperature is raised. In the absence of spin-lattice broadening, which is aided by the large spin-orbit coupling constant of W(V), we should expect to see intraionic exchange narrowing of the resonance line as the temperature is raised. In practice, spin-lattice broadening becomes the dominant effect at higher temperatures and no resonance is observable at room temperature or above. If it is assumed that the line widths at 77°K are governed solely by electron exchange, then the lifetime of an electron on a particular tungsten is ca.  $10^{-8}$  sec at this temperature.

(37) Stonehart, *et al.*, studied solutions of  $\text{Na}_2\text{WO}_4$  ( $5.0 \times 10^{-2} M$ ) in 1  $M$   $\text{H}_3\text{PO}_4$ . Although these solutions undoubtedly contain  $\text{PW}_{12}\text{O}_{40}^{3-}$ , comparison of the extinction coefficients reported by these workers for the one-electron blue with those in Table II indicates incomplete (ca. 80%) conversion of the tungsten to that particular heteropolyanion.

(38) D. P. Smith, Ph.D. Thesis, Georgetown University, 1970.

(39) E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9**, 667 (1970).

(40) A. Magneli and G. Andersson, *Acta Chem. Scand.*, **9**, 1378 (1955).

(41) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. C. Williams, *J. Chem. Soc.*, 4649 (1963).

(42) The possibility of a transition from class II to class III-A character as the anions are further reduced cannot be ruled out.<sup>39</sup> Such behavior would parallel the transition from semiconductor to metal in the tungsten bronzes.

intensity, in  $\text{PW}_{12}\text{O}_{40}^{5-}$ , and the corresponding bands in oxidized tungstocobaltate and tungstoferrate are unaffected by protonation<sup>3</sup> of the anions but are sensitive to the nature of the central atom (see Table I). Taken together, these data suggest an assignment for this band (or bands in the spectra of the 2:18 anions) in terms of oxygen-to-tungsten charge transfer, the oxygen atoms being those involved in bridging the tungstens.

**Electronic Isolation of the Central Atoms.**—The central atom in the Keggin structure is bound to the tungstate network through an oxygen atom (III in Figure 4) which is simultaneously shared by three tungsten atoms. On a simple valence-bond model there can therefore be no  $\pi$ -type superexchange interaction between a paramagnetic central atom and a reduced tungsten atom. It is clear from the esr and magnetic data presented here that electrons in the two-electron blues "prefer" to pair with one another than with unpaired electrons on the central atom. In the two-electron blues of metatungstate, tungstocobaltate(II), and tungstoferrate(III) the central atoms are virtually unaffected by the presence of the extra electrons in the surrounding tungstate network. In view of this effective isolation<sup>43</sup> of the central atoms it is somewhat surprising that the esr spectrum of the

oxidized tungstoferrate anion is so sensitive to the acidity of the solvent. Presumably the anion is protonated in the acidic media and this induces slight distortions away from the regular tetrahedral geometry.

It may finally be noted that, in contrast to the tungstocobaltate(III) anion,<sup>44</sup> the iron in tungstoferrate(III) is not first reduced to the divalent state before heteropoly blue formation. This difference in behavior is due primarily to the difference in the ionization potentials of iron and cobalt and was predicted by Simmons some years ago.<sup>17</sup>

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(43) That the isolation of the central atom is not complete is shown by the slight differences in reduction potential between metatungstate and tungstocobaltate(II) ions for example.<sup>3</sup> These differences are almost exactly paralleled by shifts in the 38-kK absorption (Table I) as pointed out elsewhere: M. T. Pope, E. Papaconstantinou, G. M. Varga, Jr., and D. R. Wexell in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier Publishing Co., New York, N. Y., 1968, p 322.

(44) L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956); L. C. W. Baker, and V. E. Simmons, *ibid.*, **81**, 4744 (1959).

## Notes

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### Heteropoly Blues. V. Electronic Spectra of One- to Six-Electron Blues of 18-Metallodiphosphate Anions<sup>1</sup>

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We have elsewhere<sup>3</sup> argued on the basis of their esr, nmr, and optical spectra that the blue species formed by the addition of one and two electrons to 1:12- and 2:18-heteropolytungstates are best described as class II mixed-valence complexes.<sup>4</sup> This description implies the trapping of the added electrons on tungsten atoms, with intraionic electron transfer occurring (at 77°K) at a slow rate on the esr time scale. Such a description can be distinguished from one in which the electrons show extensive *ground-state* delocalization (class III-A). Rabette, *et al.*,<sup>5</sup> have shown by esr measurements that reduced heteropolymolybdates derived from  $[\text{SiMo}_{12}$ -

$\text{O}_{40}]^{4-}$  have essentially the same (class II) electronic structure even when they contain as many as six extra electrons (Mo(V) atoms).

We report here the optical spectra of the one- to six-electron blues of the isostructural ions  $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$  and  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ . These spectra provide, we believe, evidence for a transition to class III-A character in the heteropolytungstates.

#### Experimental Section

**Preparation of Compounds.**—The preparation and analysis of ammonium salts of  $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$  and the *A* and *B* isomers of  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$  have been described in previous papers.<sup>6,7</sup> Solutions containing the reduced species were prepared by controlled-potential electrolysis as described elsewhere.<sup>3,6,7</sup> The solutions,  $2.0 \times 10^{-5}$ – $1.0 \times 10^{-4}$  M in heteropolyanion, were made up in water acidified to pH 1.4 with sulfuric acid. A mercury cathode was used for the tungstates, and a platinum gauze cathode was used for the molybdate reductions. The progress of reduction was followed polarographically.

**Spectra.**—Reduced solutions were transferred by syringe to 0.05-cm quartz cells, previously flushed with purified nitrogen, as described elsewhere.<sup>3</sup> Spectra were recorded on a Cary 14 spectrophotometer. Reproducibility of the spectra was very good and reoxidized solutions of the six-electron blues of the heteropolytungstates gave the characteristic uv spectra<sup>3</sup> of *A*- and *B*- $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ .

#### Results and Discussion

Under the conditions of acidity used the products of

(1) Taken from the Ph.D. thesis of E. P., Georgetown University, 1968.

(2) Author to whom correspondence should be addressed.

(3) G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970).

(4) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 248 (1967).

(5) P. Rabette, C. Ropars, and J.-P. Grivet, *Compt. Rend.*, **C265**, 153 (1967).

(6) M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, **6**, 1147 (1967).

(7) E. Papaconstantinou and M. T. Pope, *ibid.*, **6**, 1152 (1967).