

It is not at all clear at this stage why these trifluorophosphine complexes should show so little difference in shielding as one varies either composition or structure. This is certainly contrary to the experience found with vanadium¹¹ and with cobalt¹⁶ (in comparing $\text{HCo}(\text{CO})_4$ with $\text{HCo}(\text{PF}_3)_4$).

In the process of doing the fluorine- and phosphorus-decoupling work, both the fluorine and phosphorus spectra of a $\text{Mo}(\text{PF}_3)_x(\text{CO})_{6-x}$ mixture was run: it is still not possible to see the spectrum of the individual components resolved from one another. The chemical shift, though present, is still small relative to the spectral broadening caused by second-order interaction.

Conclusion

⁹⁵Mo NMR spectra can be readily run given adequate sample in solution and sharp enough lines. In our case 0.3–0.5 g of sample in 25 mL of solvent (about 0.05 M) is approaching the practical limit when pulsing overnight. In the case of $\text{Mo}(\text{PF}_3)(\text{CO})_5$ or $\text{MoP}(\text{OCH}_3)_3(\text{CO})_5$, where 5–10 g of sample was present, a crude spectrum can be seen in a single pulse. It is clear that *in situ* NMR analysis of a series of $\text{Mo}(\text{PF}_3)_x(\text{CO})_{6-x}$ compounds cannot be done without use of additional techniques.

Registry No. $\text{Mo}(\text{PF}_3)(\text{CO})_5$, 45322-05-1; *cis*- $\text{Mo}(\text{PF}_3)_2(\text{CO})_4$, 45281-94-4; *trans*- $\text{Mo}(\text{PF}_3)_2(\text{CO})_4$, 15282-05-0; *fac*- $\text{Mo}(\text{PF}_3)_3(\text{CO})_3$, 15280-12-3; *mer*- $\text{Mo}(\text{PF}_3)_3(\text{CO})_3$, 15280-14-5; $\text{Mo}(\text{PF}_3)_6$, 15339-46-5; $\text{Mo}[\text{P}(\text{OCH}_3)_3](\text{CO})_5$, 15631-20-6.

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One-Electron Reduction of 18-Molybdodiphosphate and 18-Tungstodiphosphate Ions in Aqueous Solution. A Pulse Radiolysis Study

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Received May 20, 1981

Heteropoly electrolytes to molybdenum and tungsten with Keggin structure¹ (e.g., $[\text{PW}_{12}\text{O}_{40}]^{3-}$) and Dawson structure² (e.g., $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$, henceforth designated as $(\text{P}_2\text{W}_{18})^{6-}$ and $(\text{P}_2\text{Mo}_{18})^{6-}$, respectively) are known to be capable of being reduced in distinct steps without decomposition. However, whereas the reduction of tungstates can be resolved into one-electron steps, the one-electron reduction of $(\text{P}_2\text{Mo}_{18})^{6-}$ has never been reported.

For the polarographic reduction of $(\text{P}_2\text{Mo}_{18})^{6-}$ in acidic solution, the polarographic waves are pH dependent and reduction is accompanied by protonation.³ Cyclic voltammetry with sweep rates up to 120 V s⁻¹ did not reveal intermediate (one, three, and five) electron reduction products.^{3b} For $(\text{P}_2\text{W}_{18})^{6-}$, the polarographic work has shown that reduction is not accompanied by protonation; in these experiments, the one-electron heteropoly blue is stable in the absence of oxygen for hours. Now, electrodes are multielectron donors and the nearly simultaneous addition of two electrons is possible if the two steps have similar values of the redox potentials.

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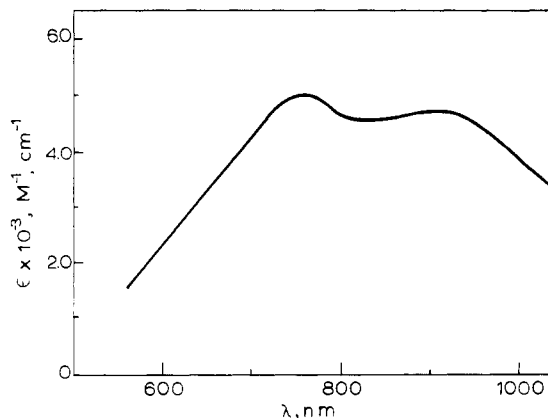


Figure 1. Spectrum of the one-electron reduction product from the reaction of $(\text{CH}_3)_2\text{COH}$ with $(\text{P}_2\text{W}_{18})^{6-}$ at pH 2 in 0.1 M $(\text{CH}_3)_2\text{CHOH}$.

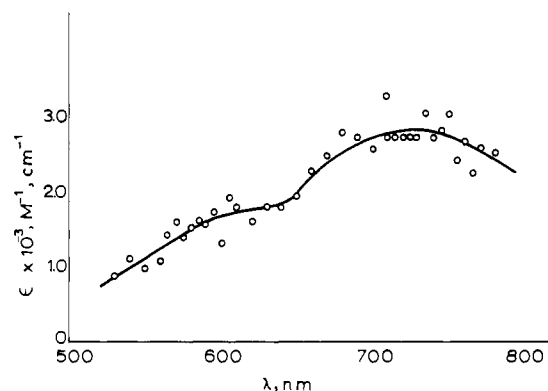


Figure 2. Spectrum of the one-electron reduction product from the reaction of $(\text{CH}_3)_2\text{COH}$ with $(\text{P}_2\text{Mo}_{18})^{6-}$ at pH 2 in 0.5 M $(\text{C-H}_3)_2\text{CHOH}$.

The technique of pulse radiolysis permits the rapid generation of reducing agents that are capable of only one-electron transfer and the detection of the reduction products by optical spectrophotometry. In this way, the one-electron reduction product of $(\text{P}_2\text{Mo}_{18})^{6-}$ can be generated, characterized, and compared with that of $(\text{P}_2\text{W}_{18})^{6-}$. It should be noted that although the ESR spectrum of the one-electron blue from $(\text{P}_2\text{W}_{18})^{6-}$ has been recorded, no corresponding spectrum from reduced $(\text{P}_2\text{Mo}_{18})^{6-}$ in aqueous solution has been obtained.⁴

Experimental Section

Literature methods⁵ were used for the preparation of $(\text{P}_2\text{Mo}_{18})^{6-}$ and $(\text{P}_2\text{W}_{18})^{6-}$; no dioxane was used in the recrystallizations in order to avoid the presence of adsorbed dioxane,⁶ which interferes with the experiments. All chemicals were analytical grade, and distilled water was further treated by passage through a Millipore purification train.

The Febretron 705 pulse-radiolysis apparatus with optical absorption spectrophotometry detection at the U.S. Army Natick Research and Development Command, which delivers a 30-ns pulse of 2.3-MeV electrons, has been previously described.⁷ Radiation dosimetry was performed with 0.1 M KSCN, taking $\epsilon_{500} 7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for the $(\text{SCN})_2^-$ radical.⁸

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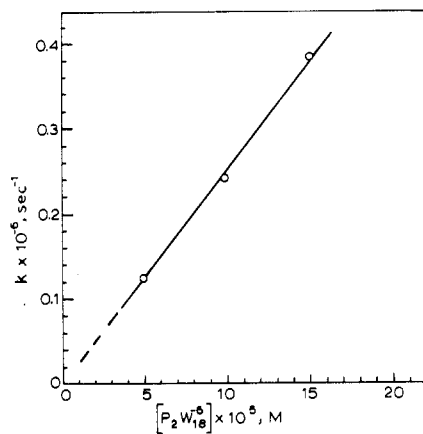


Figure 3. Dependence of the pseudo-first-order rate constant for the formation of the one-electron reduction product from (P₂W₁₈⁶⁻) on [substrate] (CH₃OH, 0.5 M, in 0.1 M HClO₄).

Table I. Rate Constants for the Reaction of α Radicals with Heteropolyanions^a

radical	10 ⁻⁹ k, M ⁻¹ s ⁻¹ ^b	
	(P ₂ W ₁₈ ⁶⁻)	(P ₂ Mo ₁₈ ⁶⁻)
·CH ₂ OH	2.6	3.7
CH ₃ ·CHOH	4.1	4.4
(CH ₃) ₂ ·COH	5.7	3.9

^a Solution medium 0.5 M alcohol, pH 2, 22 °C. ^b Experimental error ±10%.

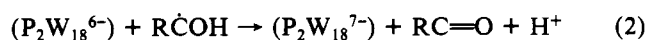
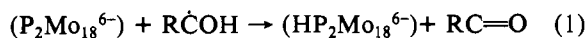
Solutions of the heteropolyanions (~10⁻⁴ M) in ~0.5 M methanol, ethanol, or 2-propanol were saturated with N₂O (2.5 × 10⁻² M). For stability reasons, solutions of (P₂Mo₁₈⁶⁻) were adjusted to pH ~2 with HClO₄.

Interaction of high-energy electrons with water in dilute aqueous solutions produces e_{aq}⁻, ·OH, and H as the radical species with *G* values (number of molecular species produced/100 eV of energy absorbed) of 2.8, 2.8, and 0.55, respectively. In acidic solutions and the presence of N₂O, e_{aq}⁻ are transformed to H and ·OH; in the presence of CH₃OH, CH₃CH₂OH, and (CH₃)₂CHOH, H and ·OH engage in H-abstraction reactions to form the one-electron reducing radicals (·CH₂OH, CH₃·CHOH, and (CH₃)₂·COH, respectively). Thus, in <1 μs, all the primary radicals have been converted virtually quantitatively to the alcohol radicals.

Results and Discussion

The reaction of the α -carbon alcohol radicals with (P₂W₁₈⁶⁻) and (P₂Mo₁₈⁶⁻) in aqueous solution at 22 °C yields the corresponding heteropoly blues, the spectra of which are fully developed in 10–15 μs (Figures 1 and 2). The formation of the blue solution occurs via pseudo-first-order kinetics, the rate constant of which is dependent on the concentration of the substrate (Figure 3). Table I shows the second-order rate constants for the reduction of (P₂W₁₈⁶⁻) and (P₂Mo₁₈⁶⁻) by the alcohol radicals; the rate constants are at or near the diffusion-controlled limit demonstrating the exergicity of the reaction.

Reactions 1 and 2 represent the reduction of the hetero-



polyanions by the α -radicals (R·COH) in acidic solution to form the protonated reduced-molybdenum blue (HP₂Mo₁₈⁶⁻) and the unprotonated reduced-tungsten blue (P₂W₁₈⁷⁻). Although the spectrum of (P₂W₁₈⁷⁻) is stable over the longest time frame of observation (5 min), the spectrum of

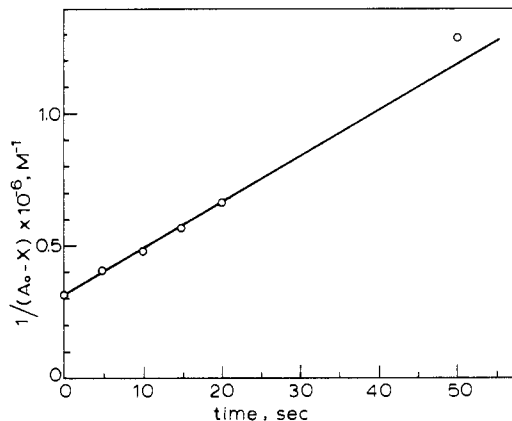


Figure 4. Kinetics of the secondary absorbance change of the one-electron reduction of (P₂Mo₁₈⁶⁻): monitoring wavelength = 750 nm, optical path length = 2 cm.

(HP₂Mo₁₈⁶⁻) is stable only in the sub-second time frame; at longer times, a further increase in absorption occurs leading to a stable solution. This slow absorption increase over the course of about 1 min follows second-order kinetics (Figure 4) and is attributed to disproportionation reaction 3, where



(H₂P₂Mo₁₈⁶⁻) represents the two-electron reduced and protonated blue; the final stable absorption shows ϵ_{750} 1.6 × 10⁴ M⁻¹ cm⁻¹. Using this value and ϵ_{750} 2.8 × 10³ M⁻¹ cm⁻¹ for (HP₂Mo₁₈⁶⁻), we evaluate the rate constant of reaction 3 as 2*k* = 2.0 × 10⁴ M⁻¹ s⁻¹.

The spectra of (HP₂Mo₁₈⁶⁻) and (P₂W₁₈⁷⁻) are characterized, as is generally the case with reduced heteropoly electrolytes,⁹⁻¹¹ by two absorption bands; the band with λ_{max} ≈ 750 nm is attributed to intervalence charge transfer within the same Mo₃O₁₃ group while the weaker band at ~600 nm arises from a d-d transition. Experimental limitations prevented the recording of the spectra beyond 800 nm, where the blues absorb due to intervalence charge transfer involving two Mo₃O₁₃ groups. It has been noted that the ϵ values of the intervalence bands of the heteropoly blues are roughly proportional to the number of electrons added to the anion.⁴ It would be expected, therefore, that ϵ for (HP₂Mo₁₈⁶⁻) be approximately half that of (H₂P₂Mo₁₈⁶⁻); in fact, the known value of ϵ_{756} for (H₂P₂Mo₁₈⁶⁻) is 1.1 × 10⁴ M⁻¹ cm⁻¹, obtained from the stoichiometric reduction of (P₂Mo₁₈⁶⁻) with Cr²⁺ or controlled-potential electrolysis.¹¹ These discrepancies may be due to differences in the solution medium and distortions in the P₂Mo₁₈ structure.¹² In that respect it should be noted, that ϵ for the b isomer of [S₁Mo₁₂O₄₀]⁴⁻ in aqueous solutions is roughly twice that of a isomer.¹³ This is also true in 1:1 dioxane-water solutions.^{3b}

Decomposition disproportionation is a general characteristic of reduced heteropoly compounds. It has been shown that (P₂Mo₁₈⁸⁻) and P₂W₁₈⁸⁻ undergo a series of disproportionations at high pH, the driving force being the rapid hydrolytic degradation of the nonreduced species.¹⁴ At low pH, the nonreduced and reduced forms of both molybdates and tungstates are stable to decomposition. The protonated odd-electron reduction products of (P₂Mo₁₈⁶⁻) disproportionate to

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give even-electron reduction products; behavior similar to that we have observed by $(\text{HP}_2\text{Mo}_{18}^{6-})$ may be exhibited by three- and five-electron blues. In contrast, the corresponding non-protonated reduced tungstates do not undergo disproportionation. The difference in the disproportionation reactivity between $(\text{HP}_2\text{Mo}_{18}^{6-})$ and $(\text{P}_2\text{W}_{18}^{7-})$ can be attributed to the effect of protonation which diminishes the negative charge on the anions reducing their mutual repulsion.

Acknowledgment. The authors wish to thank Drs. I. Taub and M. Simic of the U.S. Army Natick Research and Development Command for the use of the pulse-radiolysis instrumentation and Dr. K. Whitburn for useful discussions and comments concerning technical and scientific aspects of this work. This work was supported in part by the National Science Foundation through Grant No. CHE79-18013. E.P. (visiting professor, Boston University, 1979-1980) acknowledges financial support from the North Atlantic Treaty Organization (Sen. Sci. Grant No. B138).

Registry No. $\text{P}_2\text{Mo}_{18}^{6-}$, 57609-49-1; $\text{P}_2\text{W}_{18}^{6-}$, 12269-70-4; $\text{HP}_2\text{Mo}_{18}^{6-}$, 80612-23-3; $\text{P}_2\text{W}_{18}^{7-}$, 12504-08-4.

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An Alternate Preparation of (Trifluoromethanesulfonato)pentaamminecobalt(III) and Some New Applications

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Received August 25, 1981

Traditionally, the preparation of pentaamminecobalt(III) complexes has required reaction times of several hours at elevated temperatures (60-90 °C) because of the kinetic stability of the common cobalt(III) reactants. This precludes preparations where the ligand is thermally unstable itself or subject to oxidation by cobalt(III). However, if a good leaving group is in the coordination sphere of the cobalt(III), milder conditions can be used. This is the basis of the methods involving nitrosation of coordinated azide,¹ and alkylation of coordinated acetate,² both in poorly coordinating solvents. Most recently this principle has been exploited by Dixon et al.³ using CF_3SO_3^- as a leaving group after preparing $[(\text{NH}_3)_5\text{CoO}_3\text{SCF}_3](\text{CF}_3\text{SO}_3)_2$ (I) by dehydrochlorination of $[(\text{NH}_3)_5\text{CoCl}]\text{Cl}_2$ in anhydrous $\text{CF}_3\text{SO}_3\text{H}$.

The present report gives an alternative preparation of I which is more economical in the essentially quantitative use of $\text{CF}_3\text{SO}_3\text{H}$. The convenience of the preparations with I have been demonstrated³ for a number of compounds previously made by other methods. This advantage is shown further here by the preparation of several new compounds, two of which could not be made previously, namely, the fumaronitrile⁴ and *p*-nitrophenoxide⁵ complexes. In addition, examples are given

of preparations done in the presence of 2,6-dimethylpyridine, which is a useful additive when ligand substitution liberates a proton.

Experimental Section

Trifluoromethanesulfonic acid (Aldrich Chemical Co.) was used as supplied and handled by syringe techniques. Reagent grade acetone and sulfolane (tetramethylene sulfone or 1,1-dioxathiolane) were stored over freshly heated (120 °C) Davison 4A molecular sieves and were transferred by syringe or pipet with reasonable care to minimize exposure to atmospheric moisture. Other materials were of reagent grade and were used as supplied unless otherwise indicated. Preparations in acetone or sulfolane were done in Erlenmeyer flasks closed with rubber serum caps.

Electronic spectra were obtained on a Cary 219 spectrophotometer and NMR spectra on a Varian A56/60 spectrometer. Infrared spectra were recorded on a Nicolet FT-7000 spectrophotometer in KBr pellets and as Nujol mulls.

Aquopentaamminecobalt(III) Trifluoromethanesulfonate. To a well-stirred solution of 150 mL of concentrated aqueous ammonia and 20 mL of water were added 33 g of ammonium sulfate and 60 g of cobalt(II) sulfate heptahydrate. Then 50 mL of 30% hydrogen peroxide was added slowly while the solution was warmed on a steam bath. Heating was continued for 2 h, and then the solution was cooled and neutralized with 50% sulfuric acid. The solution was refrigerated overnight, and the red crystalline product was collected by filtration. The crude product was dissolved in 400 mL of warm water and 40 mL of concentrated ammonia. The solution was filtered and neutralized with concentrated sulfuric acid. Neutralization is indicated by the color change from reddish purple $[(\text{NH}_3)_5\text{CoOH}_2^{2+}]$ to reddish orange $[(\text{NH}_3)_5\text{CoOH}_2^{3+}]$. After the solution cooled at ice temperature for several hours, the crystalline product was collected by filtration, washed with ice cold water and methanol, and air-dried to yield 40 g of product. This product has not been characterized fully, but sulfate analysis, as BaSO_4 , and the molar extinction coefficient at 492 nm⁶ are consistent with the formula $[(\text{NH}_3)_5\text{CoOH}_2](\text{SO}_4)(\text{HSO}_4)$.

The sulfate salt was converted to the trifluoromethanesulfonate salt by treatment with the stoichiometric amount of barium trifluoromethanesulfonate. The latter was prepared by slowly adding trifluoromethanesulfonic acid to an aqueous slurry of the required amount of barium carbonate until all of the carbonate dissolved. The sulfate salt (40 g) was dissolved in 400 mL of warm water (~60 °C), and the barium trifluoromethanesulfonate solution was added slowly with stirring. The mixture was digested at 60-70 °C for about 1 h, and then cooled to room temperature. The BaSO_4 was collected by filtration on a 0.22 μm Millipore filter. The filtrate was evaporated to dryness on a vacuum line while collecting the water in a large volume trap cooled in liquid nitrogen. Any excess $\text{CF}_3\text{SO}_3\text{H}$ will be removed at this stage, and any excess $\text{Ba}(\text{CF}_3\text{SO}_3)_2$ does not affect subsequent preparations.

$[(\text{NH}_3)_5\text{CoO}_3\text{SCF}_3](\text{CF}_3\text{SO}_3)_2$. Aquopentaamminecobalt(III) trifluoromethanesulfonate loses water when heated at 100-110 °C in vacuo to yield (trifluoromethanesulfonato)pentaamminecobalt(III) trifluoromethanesulfonate (I). The dehydration step has been carried out on 5-10 g samples either in a vacuum drying tube or in a tube furnace. The dehydration seems to require 2-3 h but routinely has been done overnight to ensure completion. The product has a pinkish purple color and is reasonably stable toward hydration in air, although normally it has been stored in a dessicator over calcium sulfate.

$[(\text{NH}_3)_5\text{Co}(\text{fumaronitrile})](\text{ClO}_4)_3$. A solution of I (4 g) in sulfolane (20 mL) with $\text{CF}_3\text{SO}_3\text{H}$ (2 drops) and fumaronitrile (1.1 g) was allowed to react at room temperature for 48 h. Then the solution was added with rapid stirring to a mixture of 100 mL of 2-butanol and 500 mL of ether. The resulting solid was collected by filtration, dissolved in 30 mL of 0.1 M HCl, and precipitated by addition of 70% perchloric acid. The product was recrystallized from 0.1 M perchloric acid and then subjected to chromatography on Dowex 50 W-X2 in the H^+ form. The product was separated from impurities by elution with 2 M NaCl (pH 4.5) and removed from the resin in a batch method with 6 M HCl. Concentrated perchloric acid was added to the HCl solution to precipitate the perchlorate salt. This

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