intensity, in $PW_{12}O_{40}^{5-}$, and the corresponding bands in oxidized tungstocobaltate and tungstoferrate are unaffected by protonation[3] 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 π-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[43] 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,[44] 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.[17]

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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.[3] 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.

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Notes

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Heteropoly Blues. V. Electronic Spectra of One- to Six-Electron Blues of 18-Metallodiphosphate Anions[1]

BY ELIAS PAPACONSTANTINOU AND MICHAEL T. POPE[2]

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We have elsewhere[3] 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.[4] 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.*,[5] have shown by esr measurements that reduced heteropolymolybdates derived from $[SiMo_{12}O_{40}]^{4-}$ 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 $P_2Mo_{18}O_{62}^{6-}$ and $P_2W_{18}O_{62}^{6-}$. 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 $P_2Mo_{18}O_{62}^{6-}$ and the *A* and *B* isomers of $P_2W_{18}O_{62}^{6-}$ have been described in previous papers.[6,7] Solutions containing the reduced species were prepared by controlled-potential electrolysis as described elsewhere.[3,6,7] The solutions, 2.0×10^{-5}–1.0×10^{-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.[3] 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[3] of *A*- and *B*-$P_2W_{18}O_{62}^{6-}$.

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).

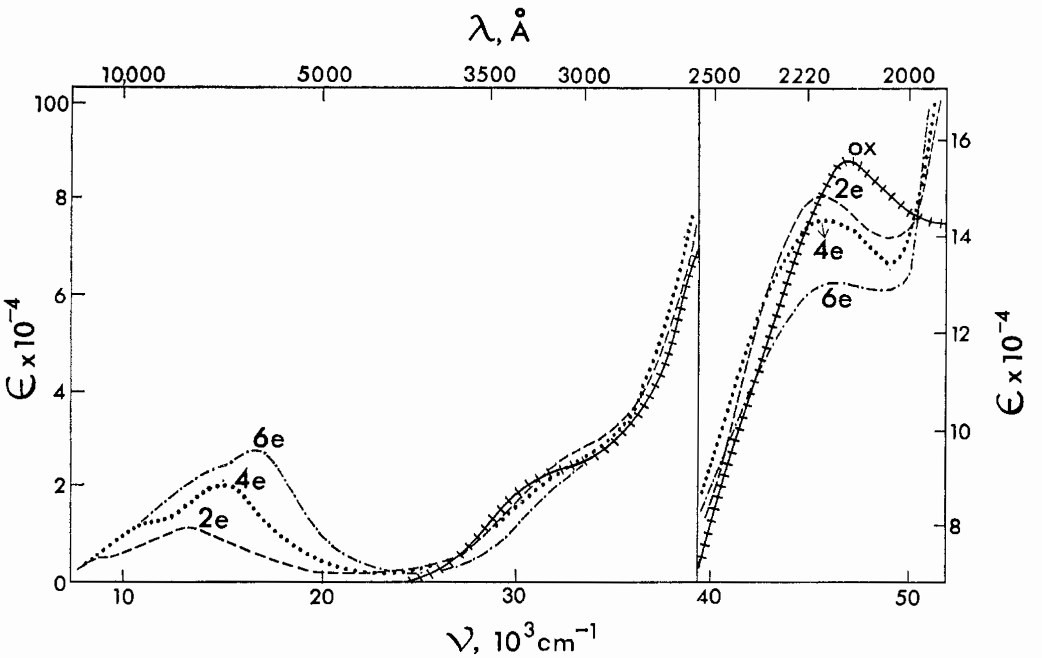

Figure 1.—Absorption spectra of $P_2Mo_{18}O_{62}^{6-}$ (ox) and its two-, four-, and six-electron blues (2e, 4e, 6e).

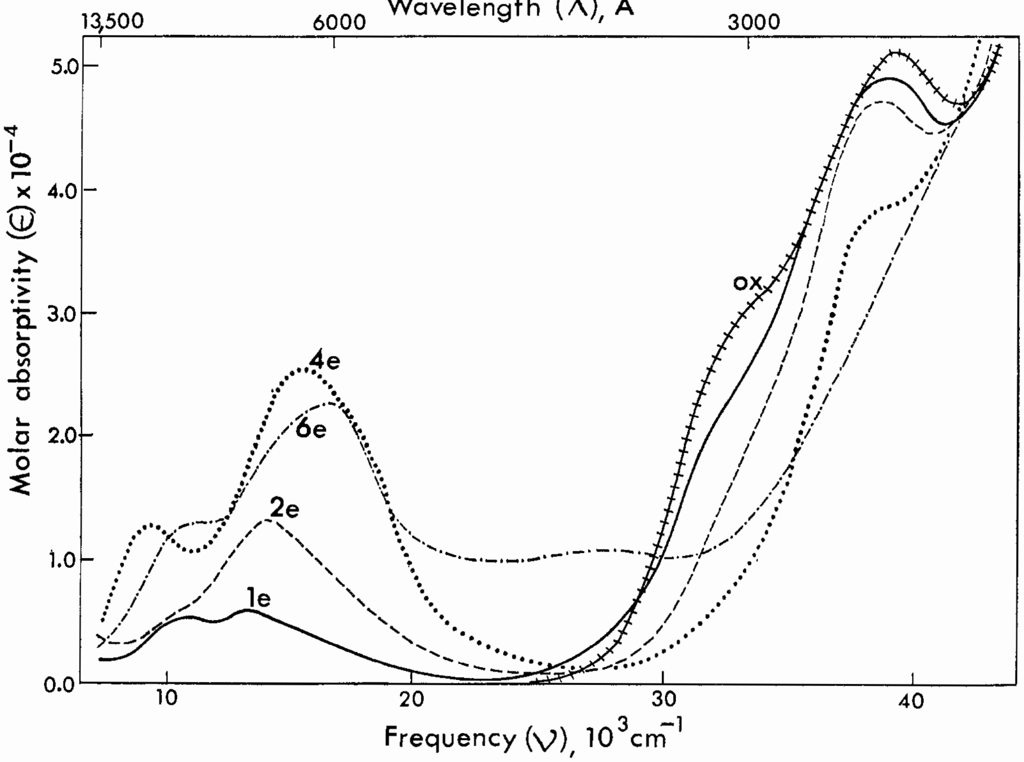

Figure 2.—Absorption spectra of A-$P_2W_{18}O_{62}^{6-}$ (ox) and its one-, two-, four-, and six-electron blues (1e, 2e, 4e, 6e).

reduction are $H_2P_2Mo_{18}O_{62}^{6-}$, $H_4P_2Mo_{18}O_{62}^{6-}$, and $H_6P_2Mo_{18}O_{62}^{6-}$ (two-, four- and six-electron blues) for the molybdates[7] and $P_2W_{18}O_{62}^{7-}$, $P_2W_{18}O_{62}^{8-}$, $H_2P_2W_{18}O_{62}^{8-}$, and $H_4P_2W_{18}O_{62}^{8-}$ (one-, two-, four-, and six-electron blues) for both isomers of the tungstates.[6] Absorption spectra of these species are illustrated in Figures 1 and 2 and positions and intensities of maxima are recorded in Table I.

The broad absorption in the 10–16-kK region is similar in shape and intensity for both the molybdates and the tungstates. With the notable exception of the spectra of the six-electron tungstate blues, the maximum molar absorptivity in this region is approximately proportional to the degree of reduction (*ca.* 5000 per M(V) atom). As noted for the 12-tungstates,[3] the near-uv absorption bands, attributed to oxygen-to-tungsten charge transfer, are progressively diminished upon reduction. These data are consistent with the "trapped-valence" model referred to above.

The pronounced change noted in the spectra of the

TABLE I

SPECTRAL DATA FOR REDUCED 2:18 ANIONS IN THE VISIBLE AND NEAR-INFRARED SPECTRA

Anion	Position[a] (intensity[b]) of maxima
$H_2P_2Mo_{18}O_{62}^{6-}$	13.2 (11,000), 9.0 sh[c] (4600)
$H_4P_2Mo_{18}O_{62}^{6-}$	14.8 (19,400), 11.2 sh (12,000)
$H_6P_2Mo_{18}O_{62}^{6-}$	16.7 (27,600), 14.5 sh (23,800)
A-$P_2W_{18}O_{62}^{7-}$	13.3 (6000), 11.2 (5400)
A-$P_2W_{18}O_{62}^{8-}$	14.1 (13,100), 11.3 sh (6200)
A-$H_2P_2W_{18}O_{62}^{8-}$	15.4 (25,800), 9.5 (13,000)
A-$H_4P_2W_{18}O_{62}^{8-}$	28.0 (13,000), 16.5 (23,000), 11.2 (13,000)
B-$P_2W_{18}O_{62}^{7-}$	14.0 sh (3600), 11.0 (4400)
B-$P_2W_{18}O_{62}^{8-}$	14.4 (10,600), 10.7 sh (6600)
B-$H_2P_2W_{18}O_{62}^{8-}$	16.0 (23,300), 10.2 sh (12,200)
B-$H_4P_2W_{18}O_{62}^{8-}$	29.0 (9500), 17.1 (23,800), 10.8 sh (9100)

[a] kK; uncertainty ±0.2 kK. [b] Molar absorptivity, ±100 l. mol^{-1} cm^{-1}. [c] Shoulder.

six-electron blues of the tungstophosphates is not paralleled in the spectrum of the corresponding molybdophosphate. We suggest that this change reflects a transition to a more delocalized (class III-A) structure for the former species.[8] An analogous transition (semiconductor to metal) has been noted with the tungsten bronzes M_xWO_3 and seems to occur at x = *ca.* 0.25 for both these materials[9,10] and the related species $WO_{3-x}F_x$ and $W_{1-x}Re_xO_3$.[11] For the bronzes, where the transition metal cations are quite widely separated (*ca.* 5.4 Å), the evidence seems to be in favor of a conduction band formed through overlap of the t_{2g} orbitals of the tungsten (rhenium) atoms with the appropriate p orbitals of the oxygens.[12] According to this model, distortions of the WO_6 octahedra occur at low x values leading to a permanent electric moment and the quenching of metallic conduction. In the heteropolytungstates the tungsten atoms are closer together (*ca.* 3.4 Å) than in the bronzes and it would seem that "delocalization" of the electrons could occur through direct metal–metal orbital overlap, when the concentration of added electrons is sufficiently great. An analogous model had once been favored for the bronzes.[13]

According to its spectrum no analogous transition has occurred in the six-electron blue of $P_2Mo_{18}O_{62}^{6-}$, which is isostructural with the *B* isomer of the tungstate.[14] It is to be expected, in view of the smaller size of the 4d compared with the 5d orbitals, that transition to a class III-A species would require a higher concentration of added electrons in a polymolybdate than in an isostructural polytungstate. In support of such an argument applied to the bronzes, it may be noted that the molybdenum bronzes M_xMoO_3 become metallic only when x exceeds *ca.* 0.5. Thus $Rb_{0.27}MoO_3$ and $Rb_{0.41-0.44}MoO_3$ are both semiconductors while $K_{\sim 0.5}$-MoO_3 is metallic.[15]

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[8] An atomic structural rearrangement is unlikely in view of the fact that the blue solutions can be rapidly reoxidized without isomerization occurring, thus demonstrating the inertness of the polytungstate networks.

[9] M. J. Sienko and T. B. N. Truong, *J. Am. Chem. Soc.*, **83**, 3939 (1961).

[10] In this connection we may note that the reflectance spectra of tungsten bronzes are formally similar to those reported here in that the former show a broad absorption band which undergoes a hypsochromic shift as x increases: B. W. Brown and E. Banks, *ibid.*, **76**, 963 (1954).

[11] A. W. Sleight, *Inorg. Chem.*, **8**, 1764 (1969).

[12] J. B. Goodenough, *Bull. Soc. Chim. France*, 1200 (1965).

[13] M. J. Sienko in "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 224.

[14] Early optical crystallography indicates that the following salts [modern formulation] are isomorphous: *B*-$(NH_4)_6[P_2W_{18}O_{62}]\cdot 14H_2O$, *B*-$K_6[P_2W_{18}O_{62}]\cdot 14H_2O$, $K_6[P_2Mo_{18}O_{62}]\cdot 14H_2O$, and $(NH_4)_6[As_2W_{18}O_{62}]\cdot 14H_2O$: L. Duparc and F. Pearce, *Bull. Soc. Franc. Mineral.*, **18**, 31 (1895); *Z. Kryst.*, **27**, 612 (1897); **31**, 66 (1899).

[15] T. A. Bither, J. L. Gilson, and H. S. Young, *Inorg. Chem.*, **5**, 1559 (1966).

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Synthesis of Hexakis(thiourea)ruthenium(III)

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The reaction of ruthenium(III) with thiourea to form complex ions is of analytical importance, and much work has been done toward developing a reliable, albeit empirical, method of analysis.[1] This empirical nature inspired a theoretical study of the reaction by Yaffe and Voigt,[2] who concluded that only two complexes were present in a perchloric acid solution containing Ru(III) and thiourea. These were $RuTu^{2+}$ and $RuTu_3$. To satisfy secondary and primary valency requirements four-membered chelate rings were postulated. The thiourea was assumed to react as an acid, and evidence was presented that hydrogen ion concentration enters directly into the reaction equilibrium.

Yamaguchi and coworkers[3] studied the infrared spectra of thiourea and thiourea complexes of Pt(II) and Pd(II). They concluded that sulfur to metal bonds are found in the compounds $PtTu_2Cl_2$ and $PdTu_2Cl_2$. Valency considerations require the thiourea ligands to be neutral in these compounds.

Lebedenskii and coworkers[4,5] prepared a series of iridium and rhodium compounds in which three, four, five, or six thiourea molecules replaced a like number of chloride ions in the metal hexachlorides. Compounds containing one or two thiourea ligands could not be precipitated. The experiments indicated, however, that the reaction of thiourea with rhodium and iridium occurs in steps and any reaction solution would contain a mixture of compounds.

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[3] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *ibid.*, **80**, 527 (1958).

[4] V. V. Lebedenskii and V. S. Voldor, *Ann. Inst. Platine* (U.S.S.R.), **12**, 79 (1935).

[5] V. V. Lebedenskii, E. S. Shipiro, and N. P. Kasatkins, *ibid.*, **12**, 93 (1935).