Direct Determination by ^{183}W NMR of the Locations of Added Electrons in ESR-Silent Heteropoly Blues. Chemical Shifts and Relaxation Times in Polysite Mixed-Valence Transition-Metal Species

Mariusz Kozik, Charles F. Hammer, and
Louis C. W. Baker*

*Department of Chemistry, Georgetown University
Washington, DC 20057*

Numerous heteropoly anions[1-4] can be reduced by addition of various numbers of electrons. The reduction products, which typically retain the general structures of their oxidized parents[5] and are frequently deep blue in color, comprise a potentially important large group of complexes generally known as the "heteropoly blues". The added ("blue") electrons are "delocalized", according to various time scales, over certain atoms and/or regions of the structures. Introduction[6-9] of ^{183}W NMR for nonreduced polytungstates resulted in numerous papers and revisions of earlier conclusions derived from indirect arguments.

The present paper shows that ^{183}W NMR can also easily and directly identify the regions of diamagnetic reduced polytungstate anions wherein the blue electrons chiefly reside, and it can elucidate their effects on neighboring atoms. We are not aware of previous transition-metal NMR studies of solutions of compounds wherein several mixed-valence metal atoms are joined by bridging nonmetal atoms. Efforts to locate "blue" electrons, usually in paramagnetic 1-electron reduction products, are not new.[10-12] However, the ^{183}W NMR method has great directness and potential utility. Its focus on diamagnetic species and its longer time scale, as well as the varied availability of suitable reduction products, all complement ESR methods.

^{183}W NMR spectra[6-9] prove that unreduced α-$[P_2Mo_3W_{15}O_{62}]^{6-}$ and α-$[P_2W_{18}O_{62}]^{6-}$ have the Wells–Dawson structure[13-15] (Figure 1) and that the former complex has one Mo_3O_{13} cap. Li salts of these and the free acid of α-$[SiW_{12}O_{40}]^{4-}$ were reduced to 2-electron blues by constant-potential electrolysis.[16,17] Figure 2 shows ^{183}W NMR spectra of the reduced Wells–Dawson species. Table I gives the chemical shifts, T_1's (directly determined), and band assignments (made from relative peak areas).

The Mo atoms in Mo-substituted polytungstates are reduced preferentially,[11,18,19] and therefore the two added electrons are (paired) in the Mo_3O_{13} cap of diamagnetic α-$[P_2Mo_3W_{15}O_{62}]^{8-}$. That the three Mo atoms in the reduced species are identical is
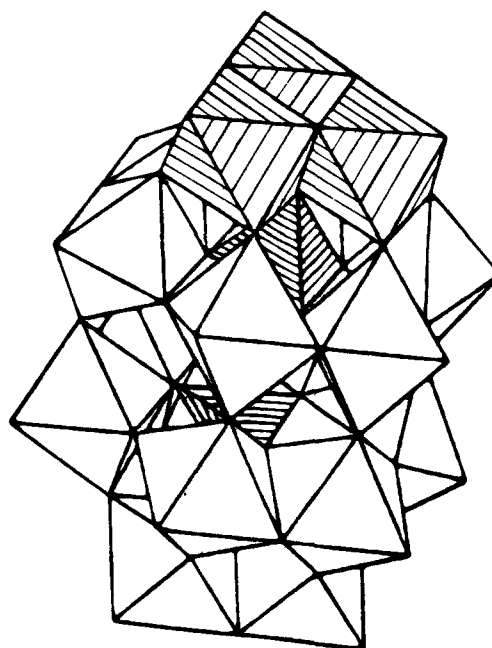
Figure 1. Wells–Dawson structure for α-$[P_2W_{18}O_{62}]^{6-}$ and α-$[P_2Mo_3W_{15}O_{62}]^{6-}$. Each vertex of a polyhedron locates the center of an oxygen atom. The P atoms are at the centers of the interior (hatched) tetrahedra. In the 18-tungsto complex, every octahedron contains a W atom, displaced toward its unshared oxygen. In $[P_2Mo_3W_{15}O_{62}]^{6-}$ three Mo atoms have replaced the W atoms in the three octahedra (hatched in this figure) which form the 3-fold cap at the top of the complex illustrated.

Table I. ^{183}W NMR Spectra of Oxidized and 2-Electron Reduced Heteropolytungstates. Data Taken on an AM-300WB NMR Spectrometer

	cap W's	belt W's near W cap	belt W's near Mo cap
α-$[P_2Mo_3W_{15}O_{62}]^{6-}$ at 26 °C (oxidized parent)			
relative areas	1	2	2
chem shifts, ppm	−134	−180	−179
α-$[P_2Mo_3W_{15}O_{62}]^{8-}$ at 26 °C (reduced species)			
relative areas	1	2	2
chem shifts, ppm	−149	−226	−238
relaxation times, ms	1300	450	100
change of chem shift ($\Delta\delta$) upon reduction, ppm	−15	−46	−59

	belt W's	cap W's
α-$[P_2W_{18}O_{62}]^{6-}$ at 26 °C (oxidized species)		
relative areas	2	1
chem shifts, ppm	−173	−127
relaxation times, ms	1750	1140
α-$[P_2W_{18}O_{62}]^{8-}$ at 26 °C (reduced species)		
relative areas	2	1
chem shifts, ppm	−51	−299
relaxation times, ms	23.4	340
change of chem shift ($\Delta\delta$) upon reduction, ppm	+122	−172

	all W's
α-$[SiW_{12}O_{40}]^{4-}$ at 26 °C (oxidized species)	
chem shift, ppm	−103
relaxation time, ms	4600
α-$[SiW_{12}O_{40}]^{6-}$ at 26 °C (reduced species)	
chem shift, ppm	−43
relaxation time, ms	28
change of chem shift ($\Delta\delta$) upon reduction, ppm	+60

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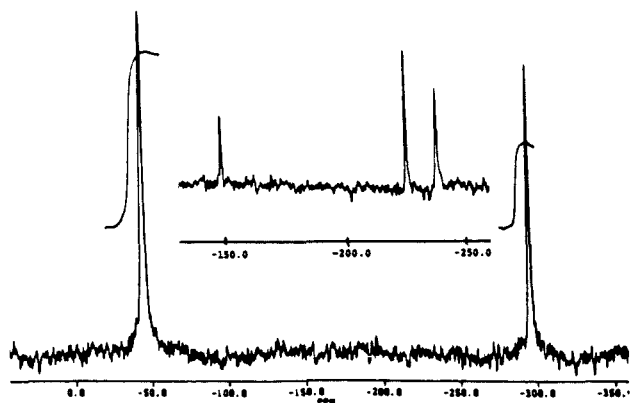(19) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3194.

shown by the spectrum's consisting of just three simple lines. Therefore the two electrons are paired and delocalized over the three Mo atoms, on the NMR time scale. As shown in Table I, all the lines are shifted upfield by the reduction. The upfield shift

Figure 2. ^{183}W NMR spectra. Upper inset: 0.15 M α-[P$_2$Mo$_3$W$_{15}$O$_{62}$]$^{8-}$ solution (2-electron reduction product); W frequency = 20.83 MHz; temperature 26 °C; chloroacetate buffer, pD 3.5. Lower spectrum: 0.20 M α-[P$_2$W$_{18}$O$_{62}$]$^{8-}$ solution (2-electron reduction product); W frequency = 12.5 MHz; temperature 26 °C; acetate buffer, pD 4.5.

and shortening of relaxation time are greatest for those W's nearest the reduced Mo cap. Those effects become steadily weaker for W's at progressively greater distances.

The single resonance ($\Delta\nu_{1/2}$ = 14 Hz) observed for the 2-electron reduction product of α-[SiW$_{12}$O$_{40}$]$^{4-}$ shows that the W complex retained the α form upon reduction and that the added electrons are delocalized over all 12 W atoms. The $\Delta\delta$ upon reduction is *downfield* (by +60 ppm), and there is a large decrease in relaxation time compared to that for the oxidized parent.[6,8]

The resonance for the 12 belt W's of α-18-tungstodiphosphate is also shifted *downfield* (by +122 ppm) by the reduction, while the resonance for the six cap W's shifts *upfield* (by -172 ppm). Thus the order of the large and small bands is reversed from that in the oxidized species.[7] In the heteropoly blue the 12-W peak ($\Delta\nu_{1/2}$ = 18 Hz) is broadened relative to the 6-W one ($\Delta\nu_{1/2}$ = 4 Hz). Most striking is the almost 14-fold faster relaxation for belt W's than for cap W's (see Table I). These data make it clear that the two spin-paired "blue" electrons in α-[P$_2$W$_{18}$O$_{62}$]$^{8-}$ are delocalized over the two 6-W *belts* of the complex, producing, as in the α-[SiW$_{12}$O$_{40}$]$^{6-}$ case, substantial *downfield* $\Delta\delta$ and greatly shortened relaxation time. On the other hand, the signal from the cap W atoms, over which the added electrons are *not* delocalized, is shifted *upfield* by the proximity of the reduced atoms. The effect on the relaxation times for those unreduced W's is much smaller, in the range observed for the unreduced W atoms in α-[P$_2$Mo$_3$W$_{15}$O$_{62}$]$^{8-}$.

The ^{183}W NMR spectrum of the 2-electron reduction product of Wells–Dawson α-[P$_2$Mo$_6$W$_{12}$O$_{62}$]$^{6-}$, wherein the W atoms occupy a "boat" configuration having two eclipsed W atoms in each cap and 4 adjacent pairs of eclipsed W atoms in the belts,[9] involves, as expected, reduction of Mo atoms only. The three 4-W lines which comprise the spectrum are all shifted upfield by the reduction.

For all of the reduced W atoms in all these complexes, temperature increase produced marked upfield chemical shifts (-1.0 to -1.5 ppm/°C) while causing very small downfield shifts (<+0.1 ppm/°C) for the nonreduced W's in all the reduced and oxidized species.

Suggested Explanations. These reduced polytungstates are completely diamagnetic.[20] ESR spectra consistent with distorted octahedral d^1 W^{5+} have been observed for the 1-electron reduction products of the Keggin and 18-tungsto complexes considered herein.[11,12,16,20] Sanchez et al.[12] estimated from ESR spectra the activation energies for electron hopping in 1-electron reduced α-12-tungstosilicate and Wells-Dawson α-18-tungstodiarsenate to be only 0.035 and 0.040 eV, respectively. Optical spectra of both 1- and 2-electron blues of α-12-tungstosilicate and of α-18-tungstodiphosphate all show the same two d–d transitions,

attributable to the existence of separate d^1 W^{5+} atoms in each complex on that extremely rapid time scale.[11,20] (An intervalence CT transition is also observed in each case.) Thus the added electrons are on different (not necessarily adjacent) W atoms at a given instant, but they hop very rapidly among those W's over which they are "delocalized" on the NMR time scale or even the ESR time scale at higher temperatures. The two electrons' spins are completely coupled at all times via a strong multiroute superexchange.

A general upfield contribution to the chemical shift for all W atoms is expected upon reduction, on the basis of increased nuclear shielding by the added electrons. This is observed directly for all W's that do not receive electrons. The hopping electrons also cause oscillations in magnetic fields, shortening the relaxation times of those nonreduced W atoms. As expected, both effects are attenuated by increasing distance from the blue electrons (cf. the 3-molybdo-15-tungstodiphosphate spectra).

To estimate the direction and approximate magnitude of the chemical shifts of those W atoms among which the electrons are hopping, we presume a weighted average of the $\Delta\delta$'s of those not possessing a blue electron at a given instant and those which do. For all of the atoms onto which electrons hop, we presume a general upfield $\Delta\delta$ of about the same magnitude as that exhibited by the cap W's in reduced 18-tungstodiphosphate. Those cap W's are also immediately adjacent to reduced W atoms). Superimposed on that upfield shift is a sizeable downfield $\Delta\delta$ for the atoms possessing the added electrons at a given instant. This downfield $\Delta\delta$ is estimated, for the "diagmagnetic d^1 W^{5+} atoms" by use of the Jameson–Gutowski equation.[8,21]

temp independent paramag. contribution to shielding =

$$\sigma P = -\frac{2e^2\hbar^2}{3m^2c^2\Delta E}\left[\left\langle\frac{1}{r^3}\right\rangle_p Pu + \left\langle\frac{1}{r^3}\right\rangle_d Du\right]$$

wherein we assume all terms are approximately constant except σP and ΔE. The latter is obtained from a weighted average[22] of the wavelengths of the two W^{5+} d–d transitions revealed by the optical spectrum. The downfield contribution to the $\Delta\delta$ is then obtained by extrapolation of the straight line plot of λ vs. δ previously determined[8] for a series of Keggin structure heteropoly tungstates. The resulting net downfield contribution for a single W^{5+} times one-sixth plus the general upfield $\Delta\delta$ times five-sixths predicts, for α-12-tungstosilicate containing 2 W^{5+}'s per 10 W^{6+}'s, an overall downfield $\Delta\delta$ of +70 ppm (experimental = +60 ppm). It is unlikely that the direction and rough relative magnitude of the shift are fortuitous although the good numerical agreement may be. The significant temperature dependence of the δ's for reduced W atoms would logically result from the nonnegligible changes in the populations of the low-lying excited states for these atoms.

In 1980 Kazanskii[23] interpreted part of the ^{17}O NMR spectrum of α-[P$_2$Mo$_{18}$O$_{62}$]$^{8-}$ as showing that its two added electrons are, even at 50 °C, "firmly trapped" on two particular adjacent Mo atoms, one from each belt of the complex. The present data do not support his proposal that an analogous situation holds for [P$_2$W$_{18}$O$_{62}$]$^{8-}$.

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