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Evaluations of a General NMR Method, Based on Properties of Heteropoly Blues, for Determining Rates of Electron Transfer through Various Bridges. New Mixed−Mixed Valence Complexes

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Abstract: Several examples of a new and potentially convenient NMR method for quantitative evaluations of electron exchange rates through various conducting molecular bridges have been investigated, with a view to elucidating some limitations and some conditions for success. This necessitated making several members of a new major general category of heteropoly complexes: the mixed−mixed valence species, wherein delocalized "blue" electrons are rapidly exchanging ($\sim 10^{-10}-10^{11}$ s^{-1}) among addenda atoms (e.g., W's) in a heteropoly entity while the same blue electrons are exchanging at a much slower rate (e.g., 10^2-10^4 s^{-1}) through the conducting bridge to another heteropoly entity. NMR spectra of heteroatoms in the bridged complex are employed. In the fast exchange region line-width analysis of the coalesced exchange peaks reveals exchange constants. In favorable cases, these may also be calculated from coalescence temperatures. In the slow exchange region, reasonable assumptions can lead to approximate values. Variations with temperature yield activation parameters. Nine bridged complexes were studied. Effects of diamagnetic, paramagnetic, rigid, and flexible bridges were investigated. Bridged complexes derived from the Keggin structure proved unsatisfactory, but derivatives of the Wells−Dawson structure gave good results. When the bridge is flexible, various countercations can hold the complex in a syn configuration, leading to anomalous exhange results; but use of hydrated Li$^+$ as the only metallic cation present allows the electrostatic repulsions of the highly charged heteropoly entities to maintain an anti configuration, which yields consistent exchange rates.

Electron transfer through various connections between different parts of molecules is of considerable current interest.[1,2] This paper presents a substantial, but far from complete, investigation of a new general method,[3] potentially comparatively easy and convenient, for making quantitative evaluations of the relative conductivities of various linkages (inorganic or organic) between entities in solution, and for revealing the activation parameters for electron exchange through those linkages. The first example of the method was communicated[3] from this laboratory in 1987. In the course of the present work various new and interesting mixed−mixed valence complexes were elucidated. These exemplify a new fundamental category of heteropoly species, for which we propose the name[3] "Kozik's salts". Kozik heteropoly complexes involve intramolecular electron transfers occurring at a certain rate among one set of atoms while the same electrons simultaneously are exchanging between other atoms of the complex at a different rate.

Organic conducting bridges have well-known significances.[4−8] Oxometalate conducting bridges, which have not been much investigated,[3] are potentially important for catalysis.[9] Heteropoly complexes connected by organic or inorganic conducting bridges are potentially important electronic materials, e.g., for design of molecular wires.[10−15]

Background

Numerous heteropoly complexes that have d^0 "addenda atoms" (e.g., W^{VI} or Mo^{VI}) within adjacent MO$_6$ octahedra that have just one unshared O atom apiece (Pope's "Type I")[16,17] can characteristically be reversibly reduced by addition of various specific numbers of electrons (at specific reduction potentials), forming intensely blue-colored complexes (the "heteropoly blues"). Typically the structures of the blue reduction products are nearly identical to those of their oxidized heteropoly parents.[18] The added "blue" electrons are delocalized by two simultaneous mechanisms:[16−21] (1) rapid thermal hopping ($\sim 10^{10}-10^{11}$ s^{-1}) among certain of the addenda atoms;

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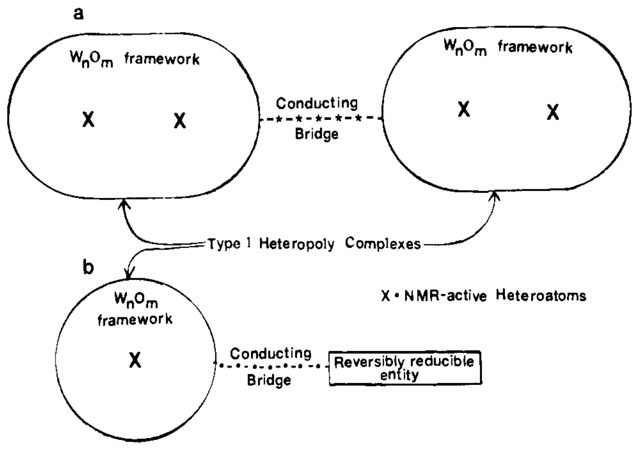

Figure 1. Schematic diagrams for (a) symmetrical bridged heteropolyanion structures and (b) similar possible bridged exchange structures using only one heteropoly end.

and (2) a ground-state delocalization involving both addenda and oxygen atoms. When a heteropoly tungstate contains an even number of blue electrons, they are always completely antiferromagnetically spin paired (completely diamagnetic). That is apparently also most usually true in the case of polymolybdates.[22]

Heteropoly entities may be linked together by a wide variety of bridges: single or multiple MO_n polyhedra[3,16,23–25] or bifunctional organic groups coordinated to transition metal heteroatoms that can be integral parts of the exterior layer of each heteropoly portion.[26–28]

General Method

First consider two identical diamagnetic heteropoly anions, each containing two of the NMR-active heteroatom, X, and linked by a symmetrical, rigid, diamagnetic conducting bridge (Figure 1a). The heteropoly entities are chosen for the ability of each to accept, at a specific reduction potential, two delocalized blue electrons.

For the fully oxidized (i.e., nonreduced) species, the X NMR spectrum consists of two lines: one for the inner pair of identical X atoms and one for the outer pair. Electrolytic reduction, at a constant potential indicated by the cyclic voltammogram, results in a four-electron-reduced species (two spin-paired blue electrons in each heteropoly entity). The X NMR spectrum of this reduced species will again be two lines, one for each structurally identical pair of X atoms, but the lines will be at modestly different chemical shifts from those of the fully oxidized complex. If the four-electron-reduced species is reoxidized by *half* the number of Coulombs that had been employed for its reduction, the solution will contain an equilibrium mixture of three bridged species: fully oxidized, four-electron reduced, and two-electron reduced. Concentrations can be chosen where intercomplex (not through the bridge) electron transfer is negligibly slow.[19] The two-electron-reduced bridged complex will contain two paired blue electrons in one heteropoly entity and none in the other. If the diamagnetic bridge is rigid, the heteropoly entities are sufficiently separated that neither of them can sense whether or not the other contains blue electrons, and if the electron exchange through the bridge is in the fast exchange region of the NMR time scale, the X NMR spectrum of the half-reoxidized solution will show two sets of three peaks each (one set for the X atoms near the bridge and the second set for the more distant pair of X atoms). In each set of three peaks, one signal is from the X atoms in the fully oxidized complex, one is from the four-electron-reduced complex, and the third peak is at a chemical shift exactly between the first two. This is the exchange peak, formed by coalescence of the signals from the oxidized and reduced ends of the two-electron species. Line-width analysis of the spectrum will reveal the electron-transfer rate through the bridge, and the variation with temperature reveals the activation parameters. Line areas show the relative concentrations of the three species. In the slow exchange region, the three bridged species present will produce only two lines for each type of X atom, coinciding with those of the oxidized and four-electron-reduced species.

The present work examined (1) four types of heteropoly entities, (2) estimation of electron transfer rates when they are in the slow exchange region of the NMR time scale, (3) effects of paramagnetic atoms in the bridge, and (4) conditions for measurement of a complex having a flexible bridge.

Compounds Used. The Na^+ salts of complexes were prepared wherein two α-$[P_2W_{15}O_{49}]$ heteropoly units are rigidly connected by a $M^{+2}{}_4O_{14}(H_2O)_2$ bridge,[24] M = Zn, Co, Ni, Cd, or Cu (Figure 2). The 15-tungsto diphosphate units were prepared by removal[29] of one W_3O_{13} cap from one end of an α-Wells–Dawson complex, α-$[P_2W_{18}O_{62}]^{6-}$ (Figure 2). The Ni_4 and Cd_4 derivatives are new compounds.

Aside from the Zn_4 complexes,[3] all blue reduction products used in the present work, including the mixed–mixed valence species, are new compounds.

Similarly, complexes were prepared containing $M^{2+}{}_4O_{14}(H_2O)_2$ bridges (M = Zn or Co) joining two B,α-$[PW_9O_{27}]$ units,[23] each derived from the α-Keggin structure by removal of one W_3O_{13} group (Figure 2).

The Li^+ salt of a complex was prepared wherein two lacunary α_2-$[P_2W_{17}O_{61}]$ units are bridged by 8-fold coordination (two tetradentate attachments) to a single Th^{4+} atom,[25] producing $[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (Figure 2). Also, two lacunary α-$[PW_{11}O_{39}]$ units were joined by similar coordination to a single Th^{4+} atom, forming[30] $[Th(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ (Figure 2).

Keggin Derivatives versus Wells–Dawson Derivatives. Although in principle it would appear that mononuclear heteropoly units, the most obvious being those derived from the Keggin structure, should give satisfactory applications of the method, and although such parent bridged complexes could be prepared and reduced to heteropoly blues, we were unable to use successfully the Zn_4-, Th-, or Co_4-bridged derivatives of the Keggin structure. In the case of the Co bridge, the

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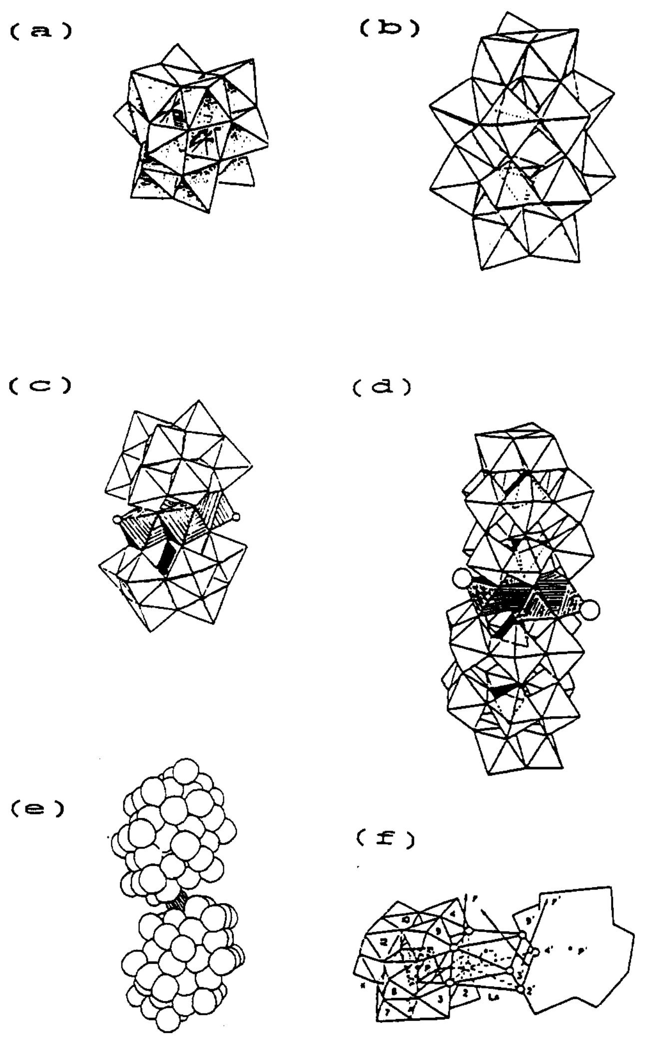

Figure 2. Some pertinent heteropolyanion structures. Each vertex locates the center of an oxygen atom. An addendum atom (e.g. W) is within each white octahedron, off-center toward the unshared vertex of the octahedron. Heteroatoms are located in the tetrahedra shown. In c and d the circles represent terminal water molecules, and the hatched octahedra contain the M^{2+} metal atoms: (a) The Keggin structure; (b) The Wells–Dawson structure; (c) The structure of $[(X^{n+}W_9O_{27})_2M^{2+}{}_4O_{14}(H_2O)_2]^{(20-2n)-}$; (d) The structure of $[(X^{n+}{}_2W_{15}O_{49})_2M^{2+}{}_4O_{14}(H_2O)_2]^{(36-4n)-}$; (e) Perspective view of *anti*-$[(\alpha_2P_2W_{17}O_{61})_2Th]^{16-}$, showing only the O atoms and the Th (hatched); and (f) the structure of $[(PW_{11}O_{39})_2M^{n+}]^{(14-n)-}$, indicating the coordination around the bridging metal. The outline on the right side of the figure represents a heteropoly end identical to the one shown on the left.

paramagnetism relaxed the ^{31}P signal to the extent that it was not observable. The reduction waves of the diamagnetic Zn_4 and Th compounds were of insufficient separation to prepare a reasonably pure four-electron-reduced species. Larger numbers of electrons were added at the same potential, producing a mixture of several reduced blue products from which no clear NMR interpretation could be made.

The derivatives of the Wells–Dawson structure, whether 15-tungsto diphosphate or 17-tungsto diphosphate, proved very satisfactory, however. In the cases of paramagnetic bridges, although the signals from the inner pair of ^{31}P atoms were rendered unobservable, the signals from the more distant pair of P atoms always proved perfectly satisfactory, and electron-transfer rates could be calculated. It has been shown that when one blue electron[22] or two blue electrons[19,21,31,32] are added to a Wells–Dawson structure, those electrons show strong preference for hopping among the W atoms of the two six-W belts of the complex (as contrasted with other W atoms of the complex), and very stable two-electron blues result.

Diamagnetic, Paramagnetic, Rigid, and Flexible Bridges. The general case when the bridge is diamagnetic and rigid (e.g., Zn_4 or Cd_4 bridges) has been explained above. When a rigid bridge contains paramagnetic atom(s) (e.g., Co_4 or Ni_4 bridges) the P atoms in one heteropoly end of the bridged complex *do* sense whether or not the other end contains blue electrons. There is substantial antiferromagnetic interaction between the paired blue electrons and the unpaired electrons of the paramagnetic atoms.[22] This changes the magnetic environments of the P atoms in the four-electron-reduced species differently from the way it changes the magnetic environment of the P atoms in the reduced end of the two-electron species. The interaction also decreases the paramagnetism[33] of the bridge, thus changing (differently) the ^{31}P resonances from the fully oxidized complex and from the oxidized end of the two-electron species. Therefore, in the fast exchange region, the coalesced exchange peak for the two-electron-reduced species will *not* be midway in chemical shift between the signals from the oxidized species and the four-electron-reduced species. Further, the spacing of the peaks will be distinctly temperature dependent. In the slow exchange region, the solution containing the three bridged species will show four peaks: one for the fully oxidized complex, one for the four-electron-reduced complex, one for the reduced end, and one for the nonreduced end of the two-electron species. In cases (e.g., the Co_4 bridge) where both the fast and slow exchange regions can be observed, reasonable assumptions about the changes with temperature of the resonances from the two-electron-reduced species can allow calculations of exchange rates.

Another circumstance which permits the P atoms in one heteropoly unit to sense whether or not the other unit contains blue electrons can occur when the bridge is sufficiently flexible that a conformation exists wherein the two heteropoly units can make close contact (e.g., the Th-bridged species). Then the exchange peak will also not be midway between the ^{31}P chemical shifts for the oxidized and four-electron-reduced species. In such cases direct exchange, not through the bridge, may also occur. These complications may be overcome, as in the case of the present Th complex, if the solution employed contains no solutes that would tend to hold the bridged species in the syn conformation. In that case the electrostatic repulsion between the high negative charges of the two heteropoly complex ends will tend to maintain an anti conformation, and the exchange peak is found exactly midway between those of the oxidized and four-electron reduced species.

Experimental Section

Synthesis and Characterization of Parent (Fully Oxidized) Heteropoly Complexes. The synthesis and purification of all of the precursors and parent complexes have been previously reported[22-25,29,30,34-37] except for the cadmium and nickel complexes. All samples were identified in the solid state by their IR spectra.[24,36,38-41]

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All of the complexes were identified and shown to be of high purity in solution by their cyclic voltammograms,[25,42] by their ^{31}P NMR spectra,[24,29,43] and, for the diamagnetic complexes, by their ^{183}W NMR spectra,[24,40] in which all peaks were observed.

Preparation of $Na_{16}[(P_2W_{15}O_{49})_2Cd_4O_{14}(H_2O)_2]$. A variation on the method described by Finke et al.[24] was used to prepare this complex. A suspension of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ was prepared in 1 M NaCl. The suspension was heated. To this suspension was added a minimal amount of solid $CdCl_2\cdot 2.5H_2O$. After heating and stirring for approximately 30 min, the solution became completely clear. This solution was allowed to cool overnight at 5 °C. Fine white crystals formed, which were filtered off and allowed to air dry.

The spectroscopic analysis and electrochemical properties indicated a pure compound isomorphous with those previously reported having a similar formula.

The ^{183}W NMR spectrum was closely analogous to that for the isomorphous Zn_4 complex.[24] The peaks occur at the following chemical shifts (in ppm): −150, −157, −166, −177, −182, −239, −242, and −243. The relative intensities correspond to those in the spectrum of the Zn_4 complex (1:2:2:2:2:2:2:2). This clearly indicates that the peak at $\delta = -150$ ppm is for the structurally unique cap tungsten atom, since it is the only position which corresponds to a relative intensity of 1. The pattern of all of the peaks corresponds closely to that of the Zn_4 compound. If the order of the chemical shifts is the same as for the isostructural Zn-bridged species, then the "cap" tungsten peaks appear at −150 and −166 ppm; the atoms in the six-W belt closest to the cap appear at −239, −242, and −243 ppm; and the peaks associated with the atoms in the six-W belt closest to the bridge (which are broadened near the baseline) occur at −157, −177, and −182 ppm.

The ^{113}Cd NMR spectrum also supports the proposed structure: two broad peaks with equal intensities centered at chemical shifts −49 and −79 ppm, corresponding to the two pairs of structurally distinct Cd atoms.

Preparation of $Na_{16}[(P_2W_{15}O_{49})_2Ni_4O_{14}(H_2O)_2]$. The method employed was similar to that described above for the Cd_4 complex. An aqueous suspension of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ was prepared in 1 M NaCl. The suspension was stirred and heated. To this suspension, an excess of solid $Ni(NO_3)_2\cdot 6H_2O$ was added. After heating and stirring for approximately 30 min, the solution was filtered. The clear filtrate was allowed to cool overnight at 5 °C. A mixture of green and yellow crystals formed, which were filtered off. The mixture was recrystallized slowly from water. The desired green product, comprising only a small fraction of the end products, was characterized spectroscopically and by cyclic voltammetry.

Synthesis and Characterization of the Reduced Heteropoly Complexes. The samples were reduced completely at the respective constant potentials.[32] For each of the derivatives of the Wells–Dawson structure, the reduction potential used was −0.56 ± 0.03 V vs the Ag/AgCl standard reference electrode. After transfer under inert atmosphere of a portion of the solution to an NMR tube, the remaining sample was reoxidized completely at an applied potential of 0.00 V. The sample was rereduced by half of the Coulombs needed for the reoxidation. A portion of the remaining sample was transferred under inert atmosphere to an NMR tube.

In the case of low-temperature samples, the volume of the portion transferred was equal to the volume of a methanol/deuterium oxide (80:20 vol %) mixture that had been deoxygenated in the NMR tube, which resulted in 40 vol % methanol solutions.

NMR Spectra. All NMR spectra were recorded on a Bruker AM-300WB spectrometer operating at a magnetic field of 7.05 T (300.10 MHz for ^1H). The spectrometer was equipped with an Aspect 3000 computer. The resonance frequency for the ^{31}P, ^{113}Cd, and ^{183}W nuclei are 121.496, 66.579, and 12.505 MHz, respectively, under these conditions. All ^{31}P spectra are relative to an 85% H_3PO_4 external standard. For the ^{113}Cd spectrum, acidified 2 M $CdCl_2\cdot 2.5H_2O$ was used as an external standard. For ^{183}W, 2 M $Na_2WO_4\cdot 2H_2O$ in D_2O was used as an external standard.

Controlled-temperature experiments utilized Bruker's Variable Temperature Unit. The probe temperatures were calibrated using the chemical shift differences in the ^1H peaks of methanol at low temperature and of ethylene glycol at high temperature as external standards.

Results and Discussion

Further Results for $Na_{16}[(P_2W_{15}O_{49})_2Zn_4O_{14}(H_2O)_2]$. As previously reported for the half-reduced samples of the Zn_4 complex,[3] for the inner and more distant isostructural pairs of P atoms, two sets of three peaks may be observed (for the oxidized, two- and four-electron-reduced species) at ambient temperatures and higher: one set (upfield) for the distant P atoms, the other (downfield) for the inner P atoms. Low-temperature studies were pursued to verify the assumptions used that the oxidized and reduced ends of the two-electron species are similar to the oxidized and four-electron-reduced species, respectively.

Samples were prepared to find the temperature of coalescence for the Zn_4 complex and to see if decoalesced peaks in the two-electron reduced species could be observed. The coalescence temperature was determined to be below 275 K, but the broadness of the exchange peaks indicates it is very close to that temperature. A methanol/water mixture (40:60 vol %; 20 vol % D_2O) was used to bring the temperature down to 250 K. The observed ^{31}P NMR spectrum contained only the peaks exactly corresponding to the oxidized and four-electron-reduced complexes. (See Figure 3.) This supports the previous assumption that the oxidized and four-electron-reduced peaks in the spectra may be used in the exchange rate calculations to represent the oxidized and reduced ends of the two-electron species.

Results for $Na_{16}[(P_2W_{15}O_{49})_2Cd_4O_{14}(H_2O)_2]$. The ^{31}P NMR spectrum observed for the Cd_4 complex is similar to that for the Zn_4 complex. The one difference is caused by $^2J_{Cd-P}$ in the downfield set of peaks (the inner P atoms). Since ^{67}Zn is only 4.11% abundant and of spin $^5/_2$, it is not surprising that analogous coupling was not observed for $^2J_{Zn-P}$.

It might be expected that the $^2J_{Cd-P}$ would be observed, since the natural abundance of ^{111}Cd and ^{113}Cd add up to 25% and both are spin $^1/_2$ nuclei. With four Cd atoms in each complex, on the average there should be one NMR-active Cd in the heteropolyanion for coupling to the P atoms. Also, there is a probability of approximately 6% for two NMR-active cadmium atoms existing in the same complex, which would be split into a 1:2:1 pattern, or 1.5% on the ends and 3.0% coinciding with the central peak. Small broadening observed in the ^{31}P NMR peaks near the baseline can be explained by this interpretation.

Using the classic analysis[44−46] for two-site chemical exchange which was applied for the Zn_4 compound,[3] the Cd_4 complex is easily analyzed. The complete set of rate constants calculated is listed in Table 1. All complexes except the Co_4 complex are calculated in this manner. Each will be discussed separately.

Results for $Na_{16}[(P_2W_{15}O_{49})_2Co_4O_{14}(H_2O)_2]$. For the complexes with paramagnetic metals in the bridge, the inner P atoms appear relaxed too quickly for ^{31}P NMR observation. When the Co_4 species was observed near room temperature (Figure

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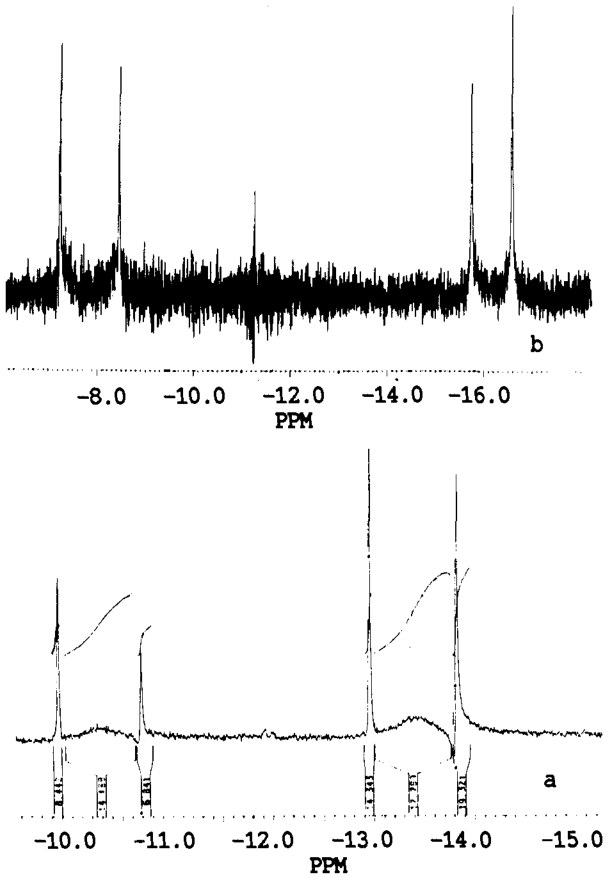

Figure 3. The ^{31}P NMR spectra for the $[(P_2W_{15}O_{49})_2Zn_4O_{14}(H_2O)_2]^{16-/18-/20-}$ mixture taken at low temperatures: (a) 5.0 mM solution (total complex concentration) of potassium salts in 1.0 M, pH = 4.7 lithium acetate buffer (20% deuterium oxide) at 277 K; (b) 2.5 mM solution (total complex concentration) of potassium salts in 40% methanol, 40% 1.25 M, pH = 4.7 lithium acetate buffer, 20% total deuterium oxide; spectrum taken at 250 K. See ref 3 for spectrum at 300 K.

4, parts b and c), the "half-reduced" sample showed only two peaks: one each for the oxidized and reduced species. As expected in the vicinity of the coalescence temperature, the baseline of the spectrum was not flat, as it had appeared in the spectra for the other isomorphous complexes, which were not near their coalescence temperatures.

When observed at higher temperatures, the spectra gained a peak between the completely oxidized and four-electron reduced peaks. This is the coalesced exchange peak for the two-electron species.

Low-temperature spectra showed the emergence of two separate decoalesced peaks for the "half-reduced" sample, which was not observed for any of the other isomorphous complexes. This compound therefore demonstrates the various conditions of the classic two-site exchange.[44-46] (See Figure 4.)

For this complex, the fast exchange region is observed only at elevated temperatures. Near room temperature (Figure 4, parts b and c), the "intermediate exchange region" is exhibited; below room temperature (281 K, Figure 4a) the exchange peak "decoalesces", demonstrating the "moderately slow exchange region".[44] Since, for the Co_4 complex, the completely oxidized peak is more downfield than the completely four-electron-reduced peak, the broad peak centered at the chemical shift of 11.5 ppm, in the 281 K spectrum, is expected to correspond to the oxidized end of the two-electron-reduced complex and, by analogy, the broad peak centered at 0.5 ppm corresponds to the reduced end of the two-electron-reduced complex (Figure 4a).

Table 1. Calculated Rate Constants

T, K	k_{ET}, s^{-1} [a]
A.For $(P_2W_{15})_2Cd_4$	
299.5	1400
313.6	3900
326.1	11000
338.6	37000
349.9	51000
B.For $(P_2W_{15})_2Ni_4$	
296.3	13000
313.8	19000
325.5	29000
338.7	65000
351.3	77000
C.For $(P_2W_{17})_2Th$ (using the Li salts)	
1. Upfield Peaks	
299.9	4800
313.8	7200
325.7	12000
338.6	35000
2. Downfield Peaks	
299.9	4100
313.8	9600
325.7	12000
338.6	32000
D.For $(P_2W_{15})_2Co_4$	
280.6	490
291.8	720
311.0[b]	4800
325.3	4900
337.0	14000
350.0	39000

[a] Calculated rate constants [b] Coalescence temperature

Unfortunately, the sample temperature cannot be lowered enough to isolate the "very slow exchange region".[44] Using Becker's suggestion[44] that the chemical shift difference varies in a predetermined manner, an assumption is made that the difference in chemical shift between the completely oxidized complex and the completely four-electron-reduced complex will be directly proportional to the difference in chemical shifts for the oxidized and reduced ends of the two-electron-reduced complex. Since the difference in chemical shift between the two ends of the two-electron-reduced complex at 281 K is 1383 Hz and the difference in chemical shift between the completely oxidized and completely four-electron reduced complexes is 736.15 Hz, the following equation is applied:

$$\Delta\nu_{2e} = \Delta\nu_{re,ox}\ (1383\ \mathrm{Hz}/736.15\ \mathrm{Hz})$$

where $\Delta\nu_{2e}$ is the calculated chemical shift difference for the two-electron reduced species at any given temperature, and $\Delta\nu_{re,ox}$ is the chemical shift difference of the oxidized and four-electron reduced species at that temperature.

Table 2 lists the chemical shifts observed for the completely oxidized and the completely four-electron-reduced Co_4 complexes. The calculated differences for the corresponding two-electron peaks are also listed. These calculated differences are used to find the set of rate constants for the Co_4 compound in the fast exchange region.

At the coalescence temperature (determined to be 311 K), the rate constant (k) is found by the equation:

$$k = \sqrt{2}\pi\Delta\nu_{2e}$$

where $\Delta\nu_{2e}$ represents the calculated chemical shift difference of the oxidized and reduced ends of the two-electron species at the coalescence temperature (calculated by the method described above).

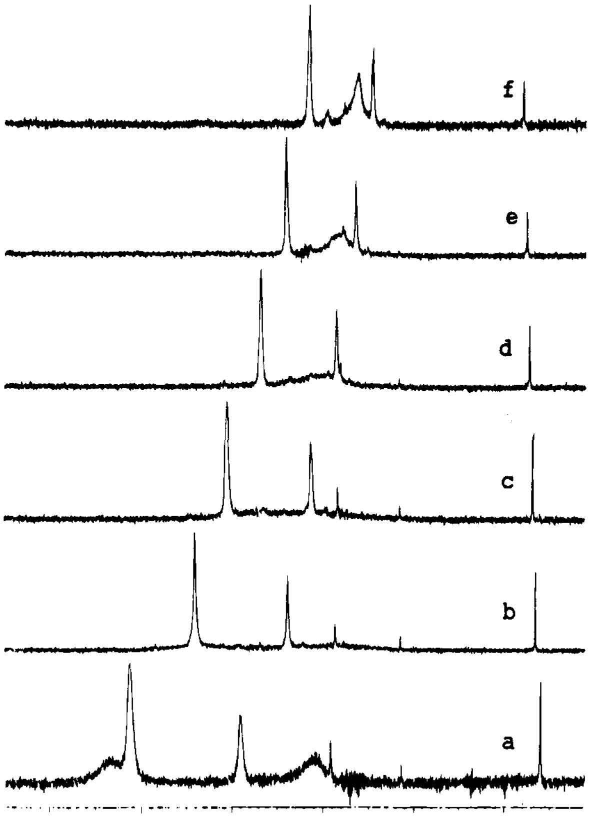

Figure 4. The ^{31}P NMR spectra for a 5.9 mM solution (total complex concentration) of the mixture of the sodium salts of $[(P_2W_{15}O_{49})_2Co_4O_{14}(H_2O)_2]^{16-/18-/20-}$ at various temperatures in 1 M, pH = 4.8 lithium acetate buffer which was 20% (volume) deuterium oxide for lock: (a) 281 K, (b) 300 K, (c) 311 K, (d) 325 K, (e) 337 K, and (f) 350 K. See Table 2. The impurity at $\delta = -14.0$ ppm (unchanging) acts as an interesting chemical shift standard, as do the more minor invariant impurities at -3.6 and -0.7 ppm.

Table 2. Estimation of the Chemical Shift Difference for the Oxidized and Reduced Ends of $[(P_2W_{15}O_{49})_2Co_4O_{14}(H_2O)_2]^{18-}$ (The Two-Electron-Reduced Cobalt-Bridged Complex)[a]

T, K	δ_{ox}[b]	δ_{red}[c]	$\Delta\nu_{re,ox}$[d]	$\Delta\nu_{2e}$[e]
280.6	1281	545	736	1383
311.0	607	37	570	1071
325.3	361	−141	502	944
337.0	182	−280	462	870
350.0	20	−406	427	803

[a] All line widths and chemical shifts reported in hertz. [b] Chemical shift of the oxidized complex. [c] Chemical shift of the four-electron-reduced complex. [d] Difference between columns 2 and 3. [e] Calculated at 280.6 K: $\delta_{2e,ox} = 1434$ Hz and $\delta_{2e,re} = 51$ Hz. Estimated at all other temperatures using the proportionality: $\Delta\nu_{2c} = (1383/736.15)\ \Delta\nu_{re,ox}$.

Finally, the rate constants calculated below the coalescence temperature are found using the equation:

$$(T_{2(obsd)})^{-1} = (T_{2(A)})^{-1} + \tau^{-1}$$

where $T_{2(obsd)}$ is the line width observed for the (broadened) exchange peak; $T_{2(A)}$ is the line width of the nonexchanging pure A; and $\tau = k^{-1}$. $T_{2(A)}$ for the oxidized and reduced ends of the two-electron complex are assumed to correspond to the T_2 observed for the completely oxidized or four-electron-reduced species, respectively. The resulting rate constants are those listed in Table 1.

Results for $Na_{16}[(P_2W_{15}O_{49})_2Ni_4O_{14}(H_2O)_2]$. When the Ni-bridged species was only "half-reduced", peaks for the oxidized, two- and four-electron-reduced species were observed for the distant P atoms in the ^{31}P NMR spectrum. The Ni-bridged complex follows an order analogous to that observed for the purely diamagnetic complexes, as is demonstrated by the relative order of the three peaks, with the most upfield peak corresponding to the fully oxidized complex.

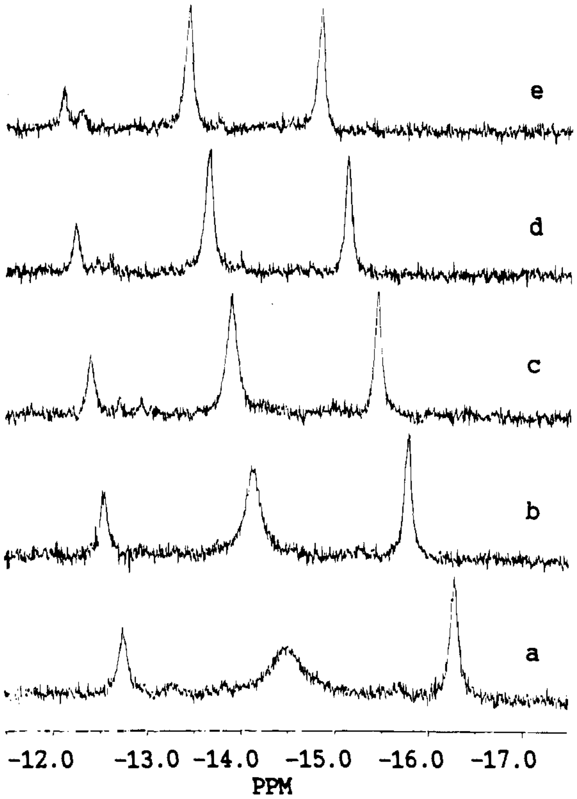

Figure 5. The ^{31}P NMR spectra for a 1.0 mM solution (total complex concentration) of the mixture of the sodium salts of $[(P_2W_{15}O_{49})_2Ni_4O_{14}(H_2O)_2]^{16-/18-/20-}$ at various temperatures in 1 M, pH = 4.7 lithium acetate buffer which was 20% (volume) deuterium oxide for lock: (a) 296 K, (b) 314 K, (c) 326 K, (d) 339 K, and (e) 351 K.

It may also be noted that the position of the exchange peak does not lie exactly between that for the oxidized and four-electron-reduced peaks at elevated temperatures. The fact that it is very close to doing so at room temperature is coincidental, since the exchange peak is the average of the chemical shifts of the oxidized and reduced ends of the two-electron-reduced species (See Figure 5.) All chemical shifts in these spectra change differently upon heating than one another and differently than the reference 85% H_3PO_4, as would be expected.

With increasing temperature, the Co_4 complex exhibits a general upfield shift of its ^{31}P NMR spectrum (Figure 4) while the spectrum of the Ni_4 complex has a general downfield shift (Figure 5). This and other differences may be explained by the isotropic and dipolar effects on the chemical shifts.[47] In octahedral Ni^{2+} complexes, there is a strong isotropic shift. The dipolar component often is negligible for these complexes. Corresponding octahedral Co^{2+} complexes usually have a strong dipolar component, which may explain chemical shift differences. Further study will be required to find the actual contributions to the chemical shift for each complex.

It is important to note the assumptions which are required to calculate the rate constants and activation parameters for the paramagnetic species: the oxidized and reduced ends of the

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(47) (a) Drago, R. S. *Physical Methods in Chemistry;* W. B. Saunders Co.: Philadelphia, PA, 1977; pp 444−446. (b) Bertini, I. and Luchinat, C. In *Physical Methods for Chemists,* 2nd ed.; Drago, R. S., Ed.; Saunders College Publishers, Philadelphia, 1992; pp 501−510.

Table 3. Summary of Rate Constants, Rates, and Activation Parameters

Complex[a]	k, s^{-1} [b]	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, eu
$(P_2W_{14})_2Zn_4$[c]	2000	43 ± 4	−37 ± 14
$(P_2W_{15})_2Cd_4$	1400	63 ± 5	+25 ± 18
$(P_2W_{15})_2Co_4$	1400	48 ± 5	−24 ± 15
$(P_2W_{15})_2Ni_4$	13000	29 ± 5	−69 ± 12
$(P_2W_{17})_2Th$[d]	4400	39 ± 5	−45 ± 15

[a] Concentrations used (mM), in order: 2.0, 4.3, 5.9, 1.0, and 2.0. First-order relationship assumed. [b] 300 K. [c] Data from ref 3. [d] Average values for rate constants found using upfield and downfield data.

two-electron species are considered similar to the completely oxidized and completely four-electron-reduced complexes for the Ni_4 complex. A special set of relationships is possible for the Co_4 complex, since there are conditions under which the two-electron species may be observed. With these requirements, it is best to consider the values for those paramagnetic species for which the slow exchange region may not be observed (e.g., the Ni_4 complex) as relative values only.

Results for $Na_{16}[(P_2W_{15}O_{49})_2Cu_4O_{14}(H_2O)_2]$. Unfortunately, deposition of Cu metal and decomposition of the complex occurred when attempts were made to produce the reduced forms of this complex.

Results for $Li_{16}[(\alpha_2\text{-}P_2W_{17}O_{61})_2Th]$. The ^{31}P NMR spectrum for the Li^+ salt of the Th complex is similar to that for the Zn_4 complex. For all temperatures from 300 to 340 K, each coalesced exchange peak is exactly centered between the resonances for the corresponding oxidized and four-electron-reduced species. Thus one heteropoly end of the complex does not sense whether or not the other end is reduced. It is therefore concluded that the complex is remaining in the anti conformation, despite the existence of the syn conformation in some other circumstances. The large, firmly hydrated Li^+ ions, present in large excess (16 per complex from the salt plus those in the 1 M lithium acetate buffer) are completely unable to hold the complex in the syn conformation, but the anti conformation is maintained by the electrostatic repulsion between the highly negatively charged heteropoly ends. The lifetime for the electron in one end of the complex, which is essentially k^{-1} for the intramolecular exchange,[3] is apparently much smaller for the Th bridge than for the M_4 bridges (Table 3).

Calculation of Activation Parameters. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ may be determined from the kinetic data using Transition State Theory.[3,48] For the Eyring plots to be linear, the reaction must be first order. (For example, see Figure 6.) It is expected that the exchange of electrons within these heteropolyanion complexes will be first order, since it is intramolecular exchange. The activation parameters are listed in Table 3.

The positive activation entropy for the Cd_4 complex was not expected, given that the other complexes have negative values and that the values for the Cd_4 and Zn_4 complexes might have been expected to be similar. No explanation is offered but the data seem clear.

Future Studies. It is probable that it will be of interest to investigate the relative conductivities of organic bridges. As one example: a Ti atom substituted into a lacunary hole of a heteropoly complex forms a very stable attachment to cyclopentadiene.[27] Organic bridges having a cyclopentadiene functional group at either end might thus form a propitious category of compounds.

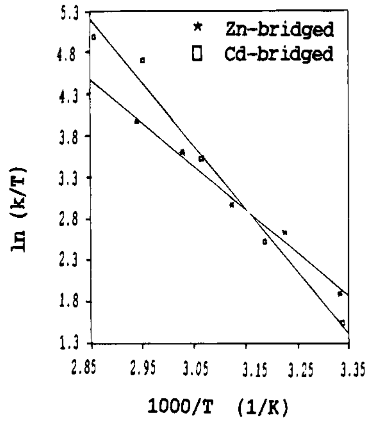

Figure 6. The Eyring plots of 1000/T vs ln (k/T), comparing the activation parameters of $(P_2W_{15})_2Cd_4$ to those of $(P_2W_{15})_2Zn_4$ (the latter from ref 3).

The compounds thus far investigated have all involved concerted exchanges of pairs of electrons. There is no apparent reason why the method cannot be applied to exchange of single electrons. It has been shown that sharp ^{31}P NMR spectra are obtained from one-electron heteropoly blues, despite their paramagnetism, because the rapid hopping of the blue electrons greatly decreases the effective correlation time. One-electron blues of the Wells–Dawson structure, having sharp ^{31}P NMR peaks, are stable.[19,20,49]

It should also be noted that in principle it is not necessary that both heteropoly units be identical or even that both contain the NMR-active heteroatom, although the proportion of reduction needed to obtain the maximum size exchange peak may vary in such nonsymmetrical cases. It is not even necessary that both ends of the bridge be attached to heteropoly units, if the nonheteropoly end is attached to an electron sink of similar reduction potential (Figure 1b).

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Supporting Information Available: All of the chemical shift and line width data for the ^{31}P NMR spectra of the samples at various temperatures (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(48) Reference 45; pp 339−341.

(49) Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 7604.