Effects of Counterions in Heteropoly Electrolyte Chemistry. 1. Evaluations of Relative Interactions by NMR on Kozik Salts

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Evidence is accumulating for the major influence of the identities of counterions on syntheses and properties of various heteropoly anions. An easy and convenient NMR method is presented for evaluating the extent of significant association between heteropoly tungstate species and monoatomic metallic counterions (e.g., alkali metal cations). In diamagnetic $[\alpha_2\text{-}P_2W_{17}O_{61}{-}Th^{4+}{-}\alpha_2\text{-}O_{61}W_{17}P_2]^{16-}$, the Th linkage is a flexible conducting bridge between the two substituted Wells−Dawson entities. A Kozik complex is a heteropoly species containing added delocalized "blue" electrons exchanging rapidly among several atoms (the belt W atoms of one Wells−Dawson unit in this case) while the same electrons exchange at a much slower rate through a conducting bridge. If a solution of the parent oxidized complex is reduced by 2 electrons per anion, the added electron pairs are distributed among the Wells−Dawson entities present, yielding an equilibrium mixture of oxidized, 4-electron-reduced, and 2-electron-reduced complexes. The ^{31}P NMR spectrum of this mixture consists, for each of the two structural types of P atoms, of three lines: one for each kind of complex. The signal for the 2-electron-reduced species, which contains a pair of electrons in one heteropoly entity and none in the other, is a coalesced exchange peak located between the other two signals. These Th complexes have anti and syn conformations. When large firmly hydrated Li^+ is the only counterion, the complex remains in the anti conformation and the exchange peak is always exactly midway between the peaks for the oxidized and 4-electron-reduced species. When even small amounts of other alkali metal cations are present, they coordinate in a pocket between the heteropoly lobes of the Th complex, holding it in the syn conformation. In the syn conformation, the P atoms in one heteropoly lobe can sense whether or not the other lobe contains added electrons. This is manifested by the exchange peak moving off-center between the signals from the oxidized and 4-electron-reduced species. The more concentrated the non-Li counterion, the greater the displacement of the coalesced signal. The order of effectiveness in the displacement is Rb > K > Na. These observations are explained, as are small changes in chemical shifts for all the species when $K(H_2O)_m{}^+$ progressively displaces $Li(H_2O)_n{}^+$ attached to the surface of the heteropoly entities. It is suggested that electron exchange through the Th and the K coordinated in the pocket adds to the stability of the syn-K Kozik complex.

Prior to about 1977 and most commonly thereafter, the identities of counterions in the reaction chemistry of heteropoly anions were essentially ignored, provided a given counterion did not cause precipitation of a reactant or product. In that year, Contant and Ciabrini[1,2] reported the important observation that $\alpha_1\text{-}[P_2W_{17}O_{61}]^{10-}$ can be prepared in solution when Li^+ is the counterion, whereas the α_2-isomer forms when other alkali metal cations are used. Since that time, scattered additional examples of the importance of the counterions in determining which products form have been reported.[2−8] Such accumulating evidence now makes it clear that the roles of counterions must be carefully considered in a sizable proportion of heteropoly reactions. Furthermore, elucidation of fundamentals of reactions of heteropoly species can be enhanced by identification and use of counterions that exhibit minimal interactions.

Knoth and Harlow[3] showed that $[P_2W_5O_{23}]^{6-}$ forms in the presence of Cs^+ while $[PW_9O_{34}]^{9-}$ results when K^+ is the counterion under identical conditions, and the use of Li^+ leads to $[PW_{11}O_{39}]^{7-}$ salts. Similarly, Contant and Tézé[4] showed that K^+ is essential to the formation of $[P_8W_{48}O_{184}]^{40-}$. Canny et al.[5] found that K^+, Rb^+, or Cs^+ stabilizes $[SiW_{10}O_{36}]^{8-}$ in solution, while its Li^+ and Na^+ salts convert readily to $\beta\text{-}[SiW_{11}O_{39}]^{8-}$ salts. Jorris et al.[6] observed that fluoro-substituted 17- and 18-tungsto species having the Wells−Dawson tungsten framework could form only in the presence of Na^+. Bas-Serra et al.[7] produced the first peroxytungstate

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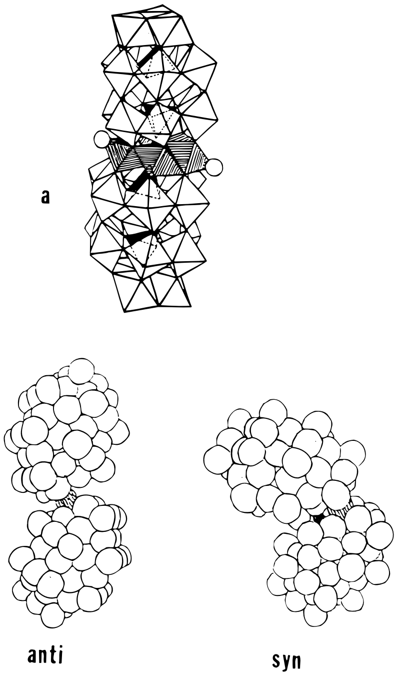

Figure 1. (a) Structure of the rigid complexes $[P_2W_{15}O_{49}-(M_4O_{16}H_4)-O_{49}W_{15}P_2]^{16-}$ (Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}). Each vertex locates the center of an oxygen atom. A W atom is within each white octahedron, off-center toward the unshared vertex of the octahedron. The four M^{2+} atoms are within the hatched octahedra. P atoms are located in the interior tetrahedra shown. The circles represent terminal water molecules coordinated to M^{2+} metal atoms. (b) Perspective views of *syn*-$[\alpha_2\text{-}P_2W_{17}O_{61}-Th^{4+}-\alpha_2\text{-}O_{61}W_{17}P_2]^{16-}$ and its *anti* isomer, showing only the O atoms, the Th atoms (hatched), and K^+ (black) holding the two heteropoly lobes in the syn conformation.

based on the Keggin structure, $\beta_3\text{-}(NH_4)_9[KCoW_{11}O_{35}(O_2)_4]\cdot 5H_2O$. In its crystal structure, the 11-tungsto entities are joined into chains by coordination of one K^+ per complex, located between adjacent complexes. The K^+ is not in the lacunary hole. When the NH_4^+ salt dissolves, one K^+ evidently remains attached to each heteropoly entity, so that the K-linked chains re-form on crystallization. Wassermann et al.[8] used the presence of Li^+ to improve the preparation of $K_{11}[A\text{-}\alpha\text{-}SiO_4W_{11}O_{35}Cr(H_2O)]\cdot 9H_2O$,[8b] while K^+ or Cs^+ is necessary[8c] for the formation of $\gamma\text{-}[SiO_4W_{10}O_{32}Cr_2(OH)(OOCCH_3)_2(H_2O)_2]^{5-}$. They also concluded that a mixture of Cs^+ and Li^+ cations is essential for the preparation of various new heteropoly species.[8a]

The present paper presents an easy and convenient NMR method to evaluate the extent of significant association of various counterions with particular heteropoly tungstate species. The present examples involve Li^+, Na^+, K^+, and Rb^+ ions, but it appears that the method should also be applicable to other monoatomic cations.

Background

In a recent paper,[9] we presented applications of Kozik salts for determination of the rates of electron transfer through various molecular bridges between heteropoly entities. Among the parent complexes surveyed were substituted Wells−Dawson tungstodiphosphate derivatives linked by coordination to monoatomic or polyatomic conducting bridges, e.g. flexible $[\alpha_2\text{-}P_2W_{17}O_{61}-Th^{4+}-\alpha_2\text{-}O_{61}W_{17}P_2]^{16-}$ and rigid $[P_2W_{15}O_{49}-(M_4O_{16}H_4)-O_{49}W_{15}P_2]^{16-}$ where $M = Zn^{2+}$, Cd^{2+}, Ni^{2+}, or Co^{2+}. See Figure 1. A Kozik complex is a heteropoly species in which added delocalized "blue" electrons are exchanging rapidly (e.g., about $10^{10}-10^{11}$ s^{-1}) among several atoms (the belt W's of one of the Wells−Dawson entities in these cases[10]) while the same electrons exchange much more slowly (e.g., about 10^3-10^4 s^{-1}) through a conducting bridge.[9] In these cases, when the number of added electrons is even, they are always completely spin paired.

Electrolytic reduction of a solution of any one of the parent complexes cited in the previous paragraph (at a constant potential determined by its cyclic voltammogram) leads to formation of a 4-electron-reduction product containing two delocalized paired electrons in each heteropoly entity.[9] Reduction by half as many coulombs results in an equilibrium mixture containing nearly statistical proportions[11] of three species: the fully oxidized complex, the 4-electron-reduced complex, and a 2-electron-reduced (Kozik) complex containing, at a given instant, two delocalized paired electrons in one heteropoly end and none in the other. Intermolecular electron exchange among the three species is negligibly slow owing to the low concentrations of the complexes.[12]

When the bridge is diamagnetic and rigid (e.g., in the Zn_4 or Cd_4 complexes cited above), the 2-electron-reduced mixture gives, in the NMR fast exchange region existing at room temperature, a ^{31}P NMR spectrum consisting of two sets of three lines each. The downfield set is for the inner pair of structurally identical P atoms, and the upfield set is for the outer pair. In each set of three peaks, one line corresponds exactly to the signal from the fully oxidized complex and one line exactly coincides with the line from the 4-electron-reduced complex. The third line is a coalesced exchange peak arising from the 2-electron-reduced species. That species, of course, contains equal amounts of reduced and oxidized heteropoly entities, exchanging the added electrons through the bridge. Line width analysis reveals that exchange rate. For a rigid diamagnetic complex, the chemical shift of each coalesced exchange peak is exactly midway between those for the signals from the corresponding P's in the fully oxidized and 4-electron-reduced forms,[9] because the equal-intensity signals that become coalesced are at exactly the chemical shifts of those two forms. That is, a P in one heteropoly entity cannot sense whether the well-separated other heteropoly entity in the same complex contains an added pair of electrons. As we have shown,[9] this last condition does not hold when the bridge contains paramagnetic atoms (e.g., in the Ni_4^{2+} or Co_4^{2+} species cited above). In such a case, the coalesced exchange peak in each three-line set is *not* midway between those of the parent fully oxidized and the 4-electron-reduced forms. That is, each coalesced exchange peak is "off-center" in its three-line set.

General Results and Interpretations

In the case of the mixture formed by the 2-electron reduction of the flexible diamagnetic Th^{4+}-bridged complex, cited above, when the only metallic cation present is Li^+, even at the high concentration used in a 1 M lithium acetate buffer (pH $\cong$ 4.7), the chemical shift of each exchange peak always remains exactly midway between the corresponding chemical shifts for the oxidized and 4-electron-reduced forms,[9] despite changes in

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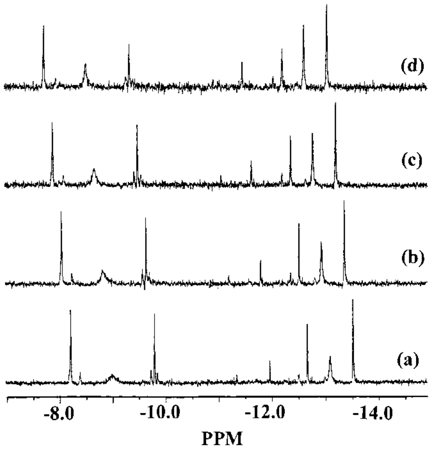

Figure 2. ^{31}P NMR spectra of the mixture formed by 2-electron reduction of a 2.0 mM solution of $Li_{16}[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ in 1 M lithium acetate buffer (pH = 4.7) containing 20% (by volume) D_2O for lock, at (a) 300 K, (b) 314 K, (c) 326 K, and (d) 339 K. (The apparent downfield shift of the whole spectrum with increasing temperature is an artifact caused by the difference in temperature effects on the sample and on the external H_3PO_4 standard, as substantiated by the constancy of the relative position of the small impurity line at −12 to −11.5 ppm.)

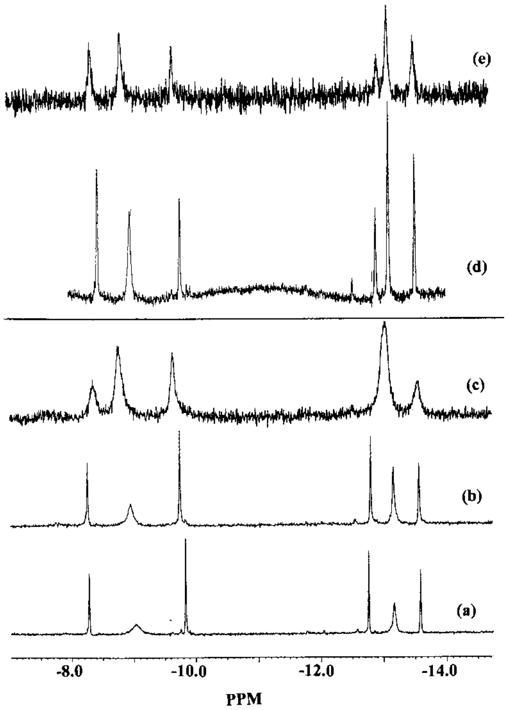

Figure 3. Comparative exchange peak displacements caused by different alkali metal cations. ^{31}P NMR spectra of mixtures, at 296 K, resulting from 2-electron reductions of $Li_{16}[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ solutions in 1 M lithium acetate buffer (pH = 4.7), containing 20% D_2O for lock: (a) 5.0 mM total heteropoly complex with Li^+ concentrations provided by 1 M lithium acetate buffer; (b) 5.0 mM total heteropoly complex concentration simultaneously 80 mM in NaCl; (c) 5.0 mM total heteropoly complex concentration simultaneously 80 mM in KCl; (d) 2.0 mM total heteropoly concentration 32 mM in KCl; (e) 2.0 mM total heteropoly concentration simultaneously 32 mM in RbCl.

concentrations and temperature. See Figure 2, and spectrum a in Figure 3.

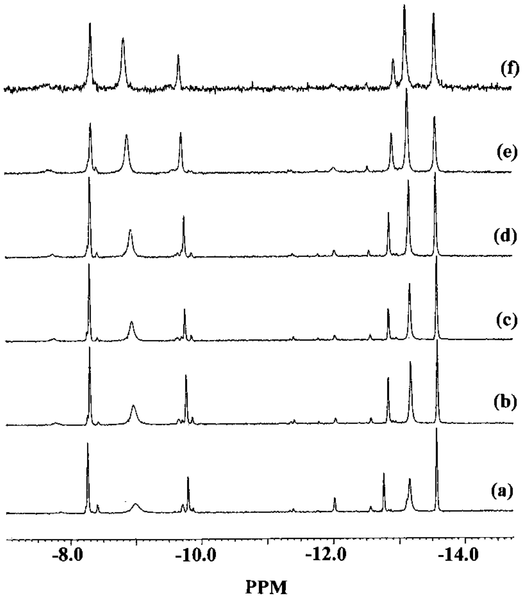

Figure 4. Comparative exchange peak displacements caused by various K^+:Th complex ratios. ^{31}P NMR spectra of mixtures resulting from 2-electron reduction of 5.0 mM $Li_{16}[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ in 1 M lithium acetate buffer (pH = 4.7), containing 20% D_2O for lock. Various amounts of KCl/LiCl mixtures were added in order to maintain constant chloride ion concentration while producing the following K^+ to total heteropoly ion ratios: (a) 0:1; (b) 1:1; (c) 2:1; (d) 4:1; (e) 8:1; (f) 10:1.

In striking contrast to the Li^+-only cases, small concentrations of Na^+, K^+, or Rb^+ (at from one to several times the total concentration of the Th species present) added to the Li Kozik salt solution in the 1 M lithium acetate buffer result in displacements of the chemical shifts of the coalesced exchange peaks from the midpoints of their respective three-line sets. The higher the concentration of added Na^+, K^+, or Rb^+, the greater such displacement. For effecting the displacement, Rb^+ is more effective than K^+, which is more effective than Na^+. Consider Figures 3 and 4.

Models indicate that the $[\alpha_2\text{-}P_2W_{17}O_{61}\text{—}Th^{4+}\text{—}\alpha_2\text{-}O_{61}W_{17}P_2]^{16-}$ complex can have two general conformations: anti and syn. See Figure 1b. In the syn conformer, the two heteropoly parts are folded into close proximity, forming a pocket between them suitable for accommodating a metal ion that joins the two tungstodiphosphate entities by coordinating to the exterior of each. See Figure 1b. In the anti conformer, the heteropoly entities are well-separated. An X-ray crystallographic study has been reported[13] for the potassium salt of the $[\alpha_2\text{-}P_2W_{17}O_{61}\text{—}Ce^{4+}\text{—}\alpha_2\text{-}O_{61}W_{17}P_2]^{16-}$ isomorph of the Th complex. Only the positions of the Ce and W atoms were determined, but these prove that the K^+ salt of this Ce complex is in the syn conformation.

The displacements of the coalesced NMR exchange peaks from the centers of their respective three-line sets in the spectra of the 2-electron reduced mixtures containing Na^+, K^+, or Rb^+ prove that in such solutions each heteropoly entity in the 2-electron reduced syn species **does** sense whether the other one contains added electrons. This is a result of the close proximity (essentially contact) of the two heteropoly lobes of the syn complex and their bridging coordination to the non-Li^+ alkali metal counterion.

The fact that the off-center displacements of the exchange peaks increase with increasing concentration of the 2-electron reduced $K_{16}[P_2W_{17}O_{61}\text{—}Th\text{—}O_{61}W_{17}P_2]$ solution (see Figure 5), when no other K^+ was added, shows that K^+ is in equilibrium with a potassium complex of the 2-electron reduced heteropoly

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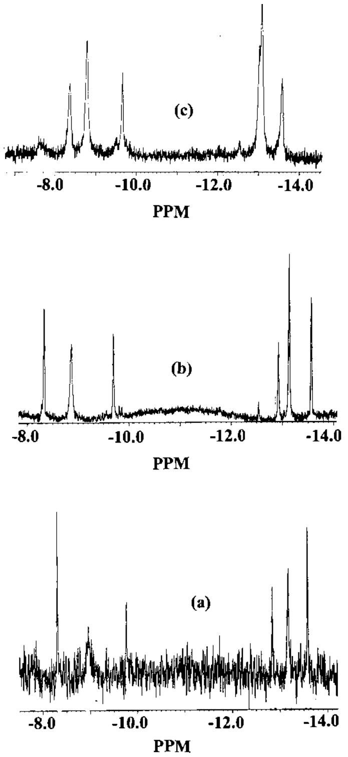

Figure 5. ^{31}P NMR spectra taken at 296 K for the mixtures formed by 2-electron reduction of $K_{16}[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ solutions of various concentrations in 1 M lithium acetate buffer (pH = 4.7), containing 20% D_2O for lock: (a) 0.5 mM; (b) 2.0 mM; (c) 5.0 mM.

species. As overall concentration increases, the following equilibrium shifts to the left: *syn*-$[K(P_2W_{17}O_{61})_2Th]^{17-} \rightleftarrows K^+ + [(P_2W_{17}O_{61})_2Th]^{18-}$ (primarily anti conformation).

The absence of exchange peak off-center displacement when Li^+ is the only metal cation leads to the conclusion that in such solutions the complex remains in the anti conformation, with the two heteropoly lobes well-separated so that neither lobe's P atoms sense whether the other lobe contains delocalized electrons. The large, firmly hydrated $Li(H_2O)_n^+$ cannot produce a coordinate link to hold the two lobes in syn conformation. In such circumstances, the high negative charges on the heteropoly lobes repel each other, maintaining the anti conformation.

Experimental Section

Preparation of Compounds. The potassium salt of $[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ was prepared by the method described by Tourné and Tourné.[14] The cyclic voltammogram agreed with the polarographic data of those authors, and the IR and ^{31}P NMR spectra agreed with those previously reported.[15,16] The lithium salt of this complex was prepared by ion exchange using a column of Dowex 50W-X8 regenerated in the Li^+ cycle.[17] The solid was obtained by vacuum evaporation of the effluent.

NMR Spectra. These were recorded on a Bruker AM-300 WB spectrometer equipped with an Aspect 3000 computer. The spectrometer operated at a magnetic field of 7.05 T (300.13 MHz for protons). An 85% H_3PO_4 solution was used as an external chemical shift standard. The spectrometer's variable-temperature unit was used with external temperature calibration by the proton signal of methanol (low temperature) or ethylene glycol (high temperature).

Preparation of Solutions of Reduced Heteropoly Complexes. Cyclic voltammograms were used to select the constant potential at which the solution of $[Th(P_2W_{17}O_{61})_2]^{16-}$ would be reduced (−0.56 ±0.03 V vs Ag/AgCl standard reference electrode). After addition of chlorides of other alkali metal ions, if any, the solutions were completely reduced (4 electrons per complex) at this potential using a BAS CV27 voltammograph with a carbon cloth working electrode, a platinum counter electrode, and an Ag/AgCl double-junction reference electrode. The coulombs used were measured with an ESC 630 coulometer. The sample, under inert atmosphere, was reoxidized completely at an applied potential of 0.00 V. Then it was rereduced under inert atmosphere by half of the number of coulombs used for the reoxidation. The resulting 2-electron-reduced mixture was transferred under an inert atmosphere to an NMR tube.

Discussion

The easily observed extents of the off-center displacements of exchange peaks in their three-line sets in the ^{31}P NMR spectra of the 2-electron reduced mixtures formed from $Li_{16}[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ solutions containing other cations provide a sensitive method for assessing the interaction of those counterions with the heteropoly complex. The method would appear to be applicable to numerous monoatomic metal cations capable of coordinating into the pocket between the heteropoly lobes of the Th complex in its syn conformation. The experiment is simple: A known amount of counterion, in lithium acetate buffer solution, is added (before or after the reduction) to an aliquot of a stock solution containing the lithium salt of the Th complex in the same buffer. The 2-electron reduction is carried out as described, and the ^{31}P NMR spectrum of the resulting solution is taken. Noncationic noncomplexing impurities should not affect the results.

It has been common to attribute the different behaviors of heteropoly species in the presence or absence of Li^+ to a supposed greater ability of the "smaller" Li^+ ion to become coordinated into the lacunary holes or other heteropoly pockets. For example, such reasoning provides the widely accepted explanation of the original observation by Contant and Ciabrini[1,2] that $\alpha_1\text{-}[P_2W_{17}O_{61}]^{10-}$ forms when the counterion is Li^+ but its α_2-isomer results when other alkali metal counterions are used because they are too large to fit into the hole so easily. Li^+ coordinated into the complex has been thought to stabilize the α_1 configuration. There is, however, no reliable evidence that the lithium is in the lacunary hole.[18]

Contrary to the foregoing widespread simplistic interpretation, the results presented in this paper strongly indicate that the Li^+ ion does *not* easily coordinate to heteropoly complexes. This suggests that differences in behavior when Li^+ is used instead of other counterions, such as observed in the α_1- and α_2-$[P_2W_{17}O_{61}]^{10-}$ cases cited above, may be better explained as depending upon Li^+ *not* coordinating to the complex. In this view, it is the α_1 species with a vacant lacunary hole that is stabilized when Li^+ is the counterion.

In considering a heteropoly complex's interaction with counterions, one must examine the whole process. While the ionic radii of Li^+, Na^+, K^+, Rb^+, and Cs^+ are respectively 0.60, 0.95, 1.33, 1.48, and 1.69 Å, the hydrated radii differ in solution

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(18) The fact that addition of K^+ to a solution of the lithium salt of the α_1 complex yields a precipitated potassium salt that, *unrecrystallized*, contains close to one Li atom per complex[1] in no way proves that Li is in or attached to the complex. Rather, it is about what would be expected if the Li^+ remains merely a counterion. Similarly, other evidence such as small changes in polarograms or absorption spectra[2] are unconvincing as evidence for incorporation of Li^+ into the anion structure.

in the reverse order: 3.40, 2.76, 2.32, 2.28, 2.28 Å.[19] The smaller the simple ion, the more firmly it attaches water molecules. The tiny Li^+ ion attaches H_2O's *much* more strongly than any of the others. Ionic hydration energies for Li^+ through Cs^+ are in the ratios 123:97:77:70:63, and transference data consequently indicate decreasing ratios of hydration numbers,[19] e.g., 25.3:16.6:10.5:...:9.9. Each factor markedly differentiates the Li^+ ion from the others.

The extraordinarily strong attachment of tiny Li^+ to the H_2O's in its first hydration layer results primarily from the large ion-induced dipole term in the attraction between Li^+ and the negative and polarizable oxygens of the waters. In contrast to those of the waters, the oxygen atoms of the heteropoly species have highly positively charged addenda (W^{VI}) atoms as nearest neighbors. The heteropoly oxygens are therefore not only far less negative than those in water molecules, but more significantly, they are very much less polarizable toward Li^+ since they are already very polarized toward the addenda. The attraction of Li^+ for heteropoly oxygens is thus very much weaker than its attraction for waters. It is decidedly energetically unfavorable for a Li^+ to leave its hydration sphere to enter into coordination to a heteropoly complex. The very stable hydrated lithium ion is of course too large to enter intact into a heteropoly pocket that would be of suitable size for a simple K^+ or other alkali metal ion.

For the alkali metal cations other than Li^+, the situation is quite different. Their hydration energies, the stabilities of their hydrated cations, and their hydrated radii are much smaller than those of Li^+, and these factors decrease with increasing size of the simple ions. That K^+ can readily coordinate in solution into a heteropoly pocket is demonstrated, for example, by the results of Bas-Serra et al.[7] described above in the second paragraph of this paper. The larger the simple alkali metal cation, the more easily it can give up its waters of hydration to enter into polydentate coordination in a heteropoly pocket. This explains the $Rb^+ > K^+ > Na^+$ order of effectiveness in displacing the exchange peaks (Figure 3).

The pronounced inward polarization of the exterior oxygen atoms of heteropoly complexes[20,21] toward the tiny highly positively charged addenda atoms beneath the surface layer of oxygens makes H-bonding to heteropoly species extremely weak. This is shown by their very low solvation energies and by the fact that heteropoly anions characteristically have hydrodynamic radii corresponding to their crystallographic radii, as shown by viscosity measurements and diffusion coefficients.[22,23]

Besides the relative tendencies of counterions to coordinate into heteropoly pockets, one must consider the general tendencies of the hydrated cations to associate with the exteriors of the negatively charged heteropoly species. In 1 M lithium acetate buffer solution, in the absence of other alkali metal cations, each negative lobe of the Th complexes used in this research was almost certainly in labile electrostatic association with several intact $Li(H_2O)_n^+$ species, in an ion-pairing fashion. As other alkali metal ions are added, the hydrated forms of these must progressively displace the $Li(H_2O)_n^+$ from positions close to the complex because hydrated radii of the other alkali metal ions are so much smaller than that of the $Li(H_2O)_n^+$. The order of displacement ability would be $Rb^+ > K^+ > Na^+ > Li^+$ on the basis of size. This interpretation is supported by an additional detailed examination of the data obtained from spectra such as those illustrated in Figure 4.

Each of the ^{31}P NMR spectra in Figures 2–5 shows six nonimpurity lines, forming, in nearly all cases, two well-separated three-line sets. (In the upfield sets of Figures 3c and 5c, two of the resonances overlap, yielding the appearance of just two lines.) The upfield set arises from the two identical P atoms farthest from the Th. That assignment is based on two observations: (1) In the oxidized complex, the environment of each of those P atoms is very nearly that of a P in α-$[P_2W_{18}O_{62}]^{6-}$, and the resonances of that upfield set are all within 1 ppm upfield from the resonance for α-$[P_2W_{18}O_{62}]$,$^{6-}$ which is at −12.7 ppm.[24] (2) It is only the downfield set that is extremely broadened when the bridge contains paramagnetic atoms.[9] The downfield set, of course, arises from the inner P atoms near the Th.

The most downfield line of the downfield set and the most upfield line of the upfield set arise from the oxidized complex, while the most upfield line of the downfield set and most downfield line of the upfield set arise from the 4-electron reduced species. The following comparisons will be made in Hz rather than ppm since the former, being smaller units, more clearly illustrate the small changes being discussed. For these spectra each ppm is 121.496 Hz.

Consider first the downfield three-line set. As the K^+:Th complex ratio steadily increases from 0:1 to 16:1 (see Figure 4), four effects are observed: (1) the frequency of the downfield (oxidized) signal decreases steadily to a point ~10 Hz upfield from that in the 0:1 ratio spectrum; (2) the frequency of the upfield (4-electron reduced) signal steadily increases, ending ~18 Hz downfield from that in the 0:1 ratio spectrum; (3) the frequency of the midpoint between these peaks consequently changes by only about 4 Hz; and (4) the frequency of the coalesced exchange peak steadily increases (shifts downfield) by about 28 Hz for the reasons discussed in previous sections.

The fact that the coalesced peak is off-center in each three-line set in the presence of Na^+, K^+, or Rb^+ is not attributable to different extents of ion pairing with those cations for the oxidized and reduced heteropoly lobes of the complex. The exchange of the added electron pair between the lobes is so rapid (~$10^{3.5}$ s^{-1}) that any shift attributable to such ion pairing remains effectively the same for each lobe. This is demonstrated experimentally by (1) the fact that the rigid Zn_4 and Cd_4 complexes, with lobes and electron exchanges very similar to those of the Th complex, never (under a variety of conditions of concentrations and temperature) produce coalesced peaks that are off-center in the respective three-line sets,[9] (2) the fact that, when Li^+ is the only cation present even in 1 M lithium acetate buffer, the flexible Th complex always shows no off-center displacement of the coalesced signal, and (3) independently by the fact that the quantitative shift data cited in the previous paragraph show that for the flexible Th complex the shifts caused by ion pairing with K^+ are much smaller (~10 and ~18 Hz between 0:1 and 16:1 K^+:heteropoly ratios) than the off-center shift of the coalesced line (~28 Hz).

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The small but steady changes in the signals from the oxidized and from the 4-electron reduced species, bringing the peaks closer together, are attributable to progressive replacement of $Li(H_2O)_n^+$ by smaller $K(H_2O)_m^+$, electrostatically held on the surface of the heteropoly lobes. This brings positive charges closer to the exterior of each heteropoly part. In the case of the 4-electron reduced complex, the added delocalized electrons have made the environment of the P atoms more negative than in the oxidized complex. The progressively increasing substitution of smaller $K(H_2O)_m^+$ units for $Li(H_2O)_n^+$ units on the exterior of the complex makes the environment of the interior P's progressively a little closer to that existing in the oxidized complex, so their chemical shifts move downfield.

The environment of an inner P in the oxidized complex differs from that in α-$[P_2W_{18}O_{62}]^{6-}$ because one neighboring $(WO)^{4+}$ unit has been removed from the shell around the P^V and replaced by just a half interest in a Th^{4+}. Increasing the positive charge of the shell by progressive substitution of attached $Li(H_2O)_n^+$ by smaller $K(H_2O)_m^+$ units acts in the direction of making that inner P's environment a little more like those in $[P_2W_{18}O_{62}]^{6-}$, which resonate at −12.7 ppm (−1543.0 Hz), which is upfield of the signal from the inner P's of the oxidized Th complex. Therefore the shift of the downfield oxidized resonance is upfield.

In the upfield three-line set, the outer P's resonance from the 4-electron reduced species also moves steadily (upfield) toward the signal from the oxidized form as $K(H_2O)_m^+$ attachment increases. The signal shifts 20 Hz upfield as the K^+:Th complex ratio goes from 0:1 to 10:1.

As the K^+:Th complex ratio increases from 0:1 to 10:1, the signal from the oxidized complex moves steadily but only very slightly downfield (1.5 Hz total), as increasing $K(H_2O)_m^+$ substitution for $Li(H_2O)_n^+$ makes the P's environment more like that in α-$[P_2W_{18}O_{62}]^{6-}$, the peak for which (−12.7 ppm) is downfield from that of the heteropoly species. In this case, the movement is very slight since the outer P's are far from the perturbation caused by the Th substitution.

The spectra in Figure 3, coupled with those in Figure 4, show, as expected, that the presence of $Na(H_2O)_p^+$ or $Rb(H_2O)_q^+$ shifts the resonances of the oxidized and 4-electron reduced signals in the same directions as those caused by $K(H_2O)_m^+$. The effect of $Na(H_2O)_p^+$ is relatively slight compared to that of $K(H_2O)_m^+$, and the effect of $Rb(H_2O)_q^+$ is more pronounced, in accordance with the proposed explanation.

Note that, in support of this interpretation, as the K^+:Th complex ratio increases, the chemical shifts for the two kinds of P atoms in the oxidized complex move in opposite directions and the chemical shifts for the two kinds of P atoms in the 4-electron reduced species also move in opposite directions. Further, in each three-line set, the chemical shifts of the oxidized and 4-electron reduced species also change in opposite directions, narrowing the three-line set in each case.

Close examination of (1) the small differences in chemical shifts, which nevertheless change very steadily and consistently over the K^+:Th complex range 0:1 to 32:1, (2) the directions of these changes, (3) the magnitudes of the changes, and (4) the magnitudes of small changes in line widths supports the foregoing ion-pairing interpretations. It must be pointed out, however, that, except for the 0:1 ratio spectrum, *all* the signals are probably to some extent peaks coalesced by exchange of syn-K-coordinate species with Th complexes containing no K^+. The central signal in each three-line set involves, when K^+ is present, coalescence based on this equilibrium as well as the electron exchange coalescence. This in no way changes the main conclusion of this paper: that the off-center shifts of the central peaks provide a sensitive means of assessing the affinities of various counterions for heteropoly tungstate species.

While the K^+ equilibrium coalescence does not enter into the assessment of electron transfer rates for the Li-only salts or for rigid complexes discussed in our previous paper,[9] it does thwart accurate assessment of electron transfer rates in the Th complex when non-Li alkali metal ions are present. Nevertheless, minimum values for the electron transfer rates in such cases may be calculated on the basis of spectra such as those in Figures 3−5, to obtain conservative values based on very conservative assumptions of corrections for line widths and chemical shifts. These indicate that the electron transfer rates substantially increase as the K^+:Th complex ratio increases. When Li^+ is the only metallic cation present, the electron exchange rate (through the Th^{4+} link) is, within experimental error, the same for the 2.0 and 5.0 mM 2-electron-reduction mixtures (e.g., as calculated from spectrum a of Figure 2 and spectrum a of Figure 4). That only the exchange through Th exists for the anti conformation is shown by the concentration independence of the exchange rate when only Li^+ ions are present. As the K^+:Th complex ratio increases to 10:1, the estimated electron transfer rate nearly triples. This is attributable to the availability in the K-syn complex of other pathways for electron exchange in addition to that through the Th link. The added delocalized electrons are concentrated in the belts of the substituted Wells−Dawson units. In the syn conformation oxygen atoms of those belts, from each lobe of the complex, are brought into contact and are coordinated to K^+, so a striking increase in electron exchange rate is not surprising.

It is probable that the stability of the 2-electron reduced K-syn complex is enhanced significantly over that of the oxidized K-syn species or the 4-electron reduced K-syn species. This interpretation is supported by comparisons of the integrated areas of the peaks as the K:(Th complex) ratio is changed. For example, in the upfield sets (Figure 4), the ratio of the area of each central exchange peak to the sum of the areas of the corresponding oxidized and 4-electron peaks rises steadily as the K:complex ratio increases: for 0:1 K to complex this ratio is 0.112; for 1:1, it is 0.152; for 2:1, 0.190; for 4:1, 0.240; for 8:1, 0.410; for 10:1, 0.496; and for 16:1, 0.659. It has been shown[21] that the two added rapidly exchanging electrons in α-$[Co^{2+}W_{12}O_{40}]^{8-}$ create an energy barrier to moving this anion's atoms away from the most favorable orbital overlap locations for the electron exchange, thereby making the complex more rigid and greatly reducing the thermal vibrations of those atoms, relative to those of oxidized α-$[Co^{2+}W_{12}O_{40}]^{6-}$, while not reducing the thermal vibrations of the atoms not in the complex. Similarly, we propose that rapid electron exchange in the Kozik K-syn species would provide an energy term contributing to stability of the complex. Any such effect would be acting to increase the sensitivity of the method with respect to detecting complexation of the alkali metal ions.

In each spectrum in Figure 4, and extending to spectra for K^+:Th complex ratios of 16:1, 20:1, 24:1, and 32:1, the midpoint between the chemical shifts of the oxidized and 4-electron reduced peaks may be calculated. The difference in Hz between that midpoint and the chemical shift of the coalesced signal can thus be obtained. A plot of these differences versus K^+:Th complex ratios shows that the difference increases linearly to about 34 Hz at the 20:1 ratio, after which the difference remains constant. This would appear to indicate that, for 5.0 mM mixtures, the 20:1 ratio is the point where essentially all of the 2-electron-reduced Kozik complex is coordinated to K^+.

The general results described in this paper also suggest the use of experiments wherein the only metal cation present is Li^+ or, when solubilities permit, counterions such as tetraalkylammonium, which cannot coordinate, whenever minimization of the complications arising from use of other counterions is sought.

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