tions for ligand binding processes are now feasible. The corresponding ability to study the thermodynamics of these processes through variable-temperature simulations offers new ways to check the validity of dynamical simulations, and to use such simulations to provide a deeper understanding of ligand binding processes.

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Ring Currents in Wholly Inorganic Heteropoly Blue Complexes. Evaluation by a Modification of Evans's Susceptibility Method

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Abstract: For seven diamagnetic heteropoly complexes, the difference between the diamagnetic susceptibility of each and that of its 2e heteropoly blue reduction product was measured by the Evans NMR susceptibility method, using a modification that yields very accurate differences. The oxidized forms of the complexes used were α-$[SiW_{12}O_{40}]^{4-}$, α-$[(H_2O)ZnSiW_{11}O_{39}]^{6-}$, α-$[P_2W_{18}O_{62}]^{6-}$, α-$[P_2Mo_3W_{15}O_{62}]^{6-}$, α-$[P_2Mo_6W_{12}O_{62}]^{6-}$, α_1-$[P_2MoW_{17}O_{62}]^{6-}$, and α_2-$[P_2MoW_{17}O_{62}]^{6-}$. In each case the 2e reduction product was *more* diamagnetic than its oxidized parent. The excess diamagnetism is attributable to a ring current of the paired delocalized "blue" electron(s) circulating, under the influence of the imposed magnetic field, in a loop in a plane with a preferred orientation perpendicular to the external field. We are unaware of other ring currents reported for discrete wholly inorganic structures. The magnitude of the additional diamagnetism caused by the ring current depends on the radius of the loop and the number of delocalized electrons circulating. The ring-current diamagnetisms are calculable by Langevin's equation, which yields values that coincide well with the experimental data. Since the delocalization of the added electrons in α-$[SiW_{12}O_{40}]^{6-}$ is almost spherical, its ring current is not dependent on the complex's orientation whereas anisotropy lowers the diamagnetic contribution of the ring current in the Zn complex and in the Wells–Dawson 18-addenda atom derivatives. In isotropic α-$[SiW_{12}O_{40}]^{6-}$ the excess diamagnetism indicates a ring-current radius of 5.4 ± 0.2 Å, which coincides with a delocalization primarily through the outer W–O shell of the complex, in accordance with evolving ^{183}W NMR data. In the Mo derivatives, Mo^{6+} is more easily reduced than W^{6+}. Thus the ring current has a small radius in α-$[P_2Mo_3W_{15}O_{62}]^{8-}$ and a large radius in α-$[P_2Mo_6W_{12}O_{62}]^{8-}$. In each monosubstituted Mo derivative, one added electron is immobilized on Mo^{5+} while the other circulates in the belt(s) of the complex. All of these effects reconcile quantitatively with the observed values, and the results can be applied to the 1e reduction products, yielding corrections to their paramagnetic moments, which make those moments consistent with one another.

Following introduction of ^{183}W NMR for study of heteropolytungstate complexes[1-5] and after important papers from other groups,[6] our laboratory initiated multinuclear NMR investigations of the "heteropoly blue" anions.[7-9] Numerous heteropoly complexes[10-15] can be reduced by addition of various numbers of electrons. The reduction products, which typically retain the general structures of their oxidized parents and are frequently deep blue in color, comprise a potentially important large group of complexes generally known as the heteropoly blues.[15-17] The added ("blue") electrons are "delocalized", according to various time scales, over certain atoms or regions of the structures.[7,18] Heteropoly blues correspond to class II systems in the Robin and Day[15,19] classification of mixed-valence compounds.

The electron delocalization is viewed as operating through two mechanisms: a thermally activated electron hopping process from one addendum (e.g., W or Mo) atom to the next and a ground-state delocalization (gsd),[16,20] presumably involving π-bonding through bridging oxygen atoms from the reduced metal atom to its neighbors. The degree of gsd has been regarded as relatively small, but its existence was required to account for intervalence charge-transfer optical absorption bands.[16] Absence of ESR signals for, and appearance of ^1H NMR signals[15,21] from, a small number of 2e reduction products (plus a semiqualitative evaluation of a magnetic susceptibility[22]) were interpreted as indicating that when there is an even number of blue electrons, their spins are characteristically paired. That postulate is greatly strengthened by a combination of recent NMR investigations[7,9,23] and the present work.

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The present paper reports, for each of seven carefully chosen 2e heteropoly blue complexes, the difference between its magnetic susceptibility in solution and that of its oxidized parent complex. In each case the blue complex was more diamagnetic than the oxidized parent by an amount that is clearly attributable to an electronic ring current of the blue electrons, set up by the applied magnetic field and thereby creating its own field in opposition to the applied field. The magnitude of the added diamagnetism coincides with the effective radius of the ring current in each case and with the number of electrons free to circulate in the ring. The ring-current contribution for each added electron having thus been evaluated, the results may be used to reconcile paramagnetic moments of 1e-reduced species.

While examples of ring currents are well-known for organic compounds,[24] we believe the present examples are the first reported for purely inorganic complexes. The fact that the delocalization of the blue electrons is essentially spherical in the α-12-tungsto heteropoly blue structure (when not in a magnetic field), while most, if not all, real, measured organic examples confine the ring current to a plane of atoms, may be of some interest theoretically.[25,26] The results indicate that the excess diamagnetism arises in the nearly spherical α-12-tungsto species from the blue electrons circulating in a plane perpendicular to the external magnetic field.

The method of measurement was an adaptation of the Evans NMR procedure.[27] As usually used, ^{1}H NMR chemical shifts are observed for a given H of a standard compound contained in solution in two coaxial NMR tubes, the outer of which also contains, in the solution, the compound of interest. Since the difference in chemical shifts depends upon the difference in volume susceptibilities for the two solutions, the magnetic susceptibility of the subject compound is calculable. Frequent sources of inaccuracies involve neglect of corrections for density differences between the two solutions (especially important for solutions of heteropoly species) and neglect of differences in solvent concentrations.

The ^{1}H NMR reference material was *tert*-butyl alcohol in the present experiments, and unusual accuracy in determining the differences in susceptibilities was attained by placing the 2e heteropoly blue in the outer tube and an equimolar solution of its oxidized parent in the inner. Thus, the usual main sources of inaccuracies as well as the relatively unpredictable[28] diamagnetic corrections for the heteropoly species were canceled. Therefore, only the magnetic effects of the *added* blue electrons were reflected by the observed chemical shift differences.

Experimental Section

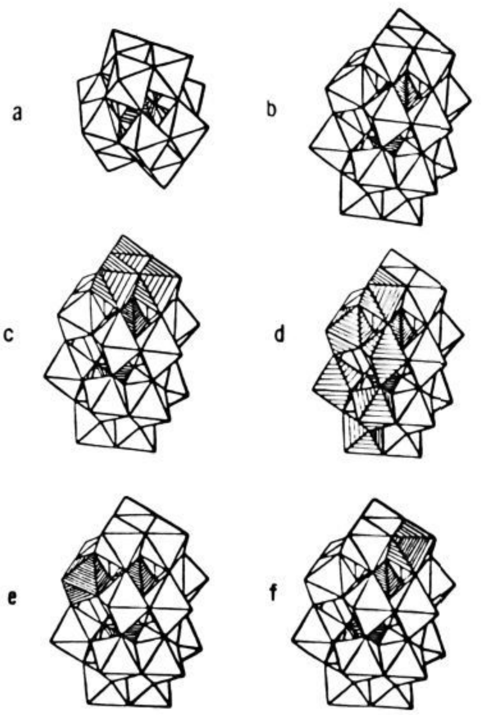

Figure 1. Structures of parent oxidized complexes. Each vertex of a polyhedron locates the center of an oxygen atom. The heteroatoms, Si^{4+} and P^{5+}, are within the central hatched tetrahedra. Within each white octahedron is a W atom, displaced significantly off-center toward the unshared oxygen atom of its octahedron. Each hatched octahedron contains a Mo atom, similarly displaced toward that octahedron's unshared oxygen atom. α-$[(H_2O)ZnSiW_{11}O_{39}]^{6-}$ has the same structure as α-$[SiW_{12}O_{40}]^{4-}$ except that one W^{6+} atom has been replaced by a Zn^{2+} atom, and the unshared coordination position of the Zn^{2+} is occupied by a H_2O molecule in place of O^{2-}: (a) Keggin structure of α-$[SiW_{12}O_{40}]^{4-}$; (b) Wells–Dawson structure of α-$[P_2W_{18}O_{62}]^{6-}$; (c) structure of α-$[P_2Mo_3W_{15}O_{62}]^{6-}$; (d) structure of α-$[P_2Mo_6W_{12}O_{62}]^{6-}$; (e) structure of α_1-$[P_2MoW_{17}O_{62}]^{6-}$; (f) structure of α_2-$[P_2MoW_{17}O_{62}]^{6-}$.

Table I. Cathodic Reduction Potentials (Epc's) for the First Two 1e CV Waves of Heteropoly Anions (V vs SCE) and the Ratios of Experimental (Q_{exptl}) and Theoretical (Q_{theor}) Numbers of Coulombs for Each Overall Electrolysis

oxidized anion	medium[a]	Epc 0–I	Epc I–II	Q_{exptl}/ Q_{theor} (for 0–II)
α-$[SiW_{12}O_{40}]^{4-}$	0.1 M HCl	−0.30	−0.51	0.95
α-$[P_2W_{18}O_{62}]^{6-}$	pH 4.0[b]	−0.05	−0.21	1.04
α-$[P_2Mo_3W_{15}O_{62}]^{6-}$	pH 2.5[c]	+0.21	+0.04	0.96
α_1-$[P_2MoW_{17}O_{62}]^{6-}$	0.3 M HCl	+0.39	−0.03	0.98
α_2-$[P_2MoW_{17}O_{62}]^{6-}$	0.3 M HCl	+0.20	−0.15	0.99
α-$[P_2Mo_6W_{12}O_{62}]^{6-}$	0.3 M HCl	+0.46[d]		0.97
α-$[(H_2O)ZnSiW_{11}O_{39}]^{6-}$	pH 4.9[b]	−0.86[d]		1.1

[a] Aqueous solutions with ≈20% D_2O added. [b] ≈1 M acetate buffer. [c] ≈1 M chloroacetate buffer. [d] 2e wave.

Synthesis and Characterization of Parent (Fully Oxidized) Heteropoly Complexes. The syntheses and purifications for the oxidized forms of all heteropoly complexes studied had been reported previously.[29-34] All samples were identified in the solid state by their IR spectra[1,35-38] and in solution by cyclic voltammetry[29,39] and ^{183}W NMR spectra.[1,2,4,5] For the tungstophosphates, ^{31}P NMR spectra[40] were also used.

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^{183}W NMR spectra have not been reported previously for the α_1 (belt-substituted) and α_2 (cap-substituted) $[P_2MoW_{17}O_{62}]^{6-}$ isomers. The spectra (17 lines and 9 lines, respectively) and their integrations[23] are precisely consistent with the proposed structures for those anions (Figure 1). In each spectrum the lines are closely spaced, in two groups corresponding to belt and cap W atoms.

Electrolytic Preparation of the Reduced Anions. Cyclic voltammograms for most of the anions studied herein had been reported previously,[29,39] but they were run again to determine the reduction potentials at the chosen conditions. Cathodic reduction potentials at the conditions used are reported in Table I for the first two 1e CV waves. The α-$[P_2Mo_6W_{12}O_{62}]^{6-}$ exhibited a 2e wave only,[29] as did $[(H_2O)ZnSiW_{11}O_{39}]^{6-}$.

Each anion was reduced by 1 or 2 electrons at a constant potential, which was below the cathodic potential of the appropriate CV wave but above the potential of the next wave. In most cases the electrolysis was stopped after the current dropped to less than 1% of the original value. In the case of $[(H_2O)ZnSiW_{11}O_{39}]^{6-}$, where the reduction was performed at a potential below −0.8 V, the criterion for discontinuing the electrolysis was the coincidence of the applied and rest potentials (−0.86 V in this case). The number of coulombs passed through the solution was recorded and compared to the theoretical number of coulombs for 100% 2e reduction, calculated from the weighed amount of heteropoly compound used, assuming the number of molecules of water of crystallization given in the literature for each compound. The small discrepancies between the theoretical and experimental numbers of coulombs probably result mainly from differences in drying procedures, which yield different numbers of molecules of water per formula in the solids used versus the samples analyzed for literature reports. The ratios of experimental and theoretical numbers of coulombs for each electrolysis are listed in Table I.

Each electrolysis was carried out with a carbon-cloth working electrode and in the presence of a Ag/AgCl double-junction reference electrode. The double-junction reference electrode was necessary to prevent precipitation of potassium salts of heteropoly anions at the contact with the electrode. The external reservoir in the double-junction electrode was filled with 1 M $LiNO_3$ solution to prevent the K^+ ions from the internal element of the electrode from coming into contact with the heteropoly anions in the electrolyzed solution. In none of the electrolyses performed was any precipitate observed, either at the standard electrode tip or in the solution. Air was rigorously excluded at all times. Nitrogen gas, having passed through a scrubbing oxygen-removal system (based on vanadous chloride), was constantly bubbled through each electrolysis solution.

Magnetic Susceptibility Measurements by the Evans Method. For each complex, 20.0 mL of 10.0 mM solution of the nonreduced heteropoly species in an appropriate buffer was prepared. The solution was divided into separate 5.0- and 15.0-mL portions. The 15.0-mL portion was reduced by 1 or 2 electrons per complex as described above, while the 5.0-mL portion remained oxidized. Both solutions were purged with pure gaseous nitrogen during the electrolysis. After the electrolytic reduction, *tert*-butyl alcohol, saturated with argon, was added to each solution, in an amount sufficient to yield a 2% solution. The nonreduced solution was transferred to the argon-swept inner NMR tube, and the reduced solution was transferred to the argon-swept outer tube. The tubes were combined together and tightly closed with Teflon tape. The ^{1}H NMR spectrum was then measured. In several cases the ^{1}H NMR spectrum was measured again after an additional delay of several hours, and there was no significant change. The NMR spectra were recorded on a Bruker AM-300WB spectrometer operating at a magnetic field of 7.05 T (300.13 MHz for protons) and equipped with an Aspect 3000 computer. Two of the complexes, α-$[SiW_{12}O_{40}]^{6-}$ and α-$[P_2Mo_6W_{12}O_{62}]^{8-}$, were also examined in a Nicolet NT-500 spectrometer operating at a magnetic field of 11.75 T (500.01 MHz for protons). The increases of diamagnetisms over those of the nonreduced complexes were identical with those measured at the lower field strength, within experimental error, demonstrating non-field-dependence of the results for the 7-12-T range.

When the inner tube contains the solution of nonreduced anion and the outer tube contains the solution of reduced anion at the same concentration and when the measurement is performed in the superconducting magnet, the difference in gram susceptibilities can be calculated[27,41] from eq 1, where $\Delta\nu$ is the difference in the frequencies of *tert*-butyl alcohol's methyl protons in the two solutions, ν_0 is the RF frequency of the ^{1}H nucleus, m is the number of grams of heteropoly salt in 1 mL

$$\chi_g(\text{blue}) - \chi_g(\text{ox}) = 3\Delta\nu/4\pi m\nu_0 \qquad (1)$$

of solution, χ_g(blue) is the gram susceptibility of the heteropoly blue, and χ_g(ox) is the gram susceptibility of the oxidized heteropoly parent. Also

$$\chi_M(\text{blue}) - \chi_M(\text{ox}) = (3\Delta\nu/4\pi\nu_0 C) \times 10^6 \qquad (2)$$

where χ_M's are molar susceptibilities and C is the concentration of each heteropoly species in millimoles per liter. According to these equations, the signal from the less diamagnetic solution will appear at more positive frequencies than the signal from the more diamagnetic solution.

Table II. Magnetic Susceptibility Data for 1e-Reduction Products at 25 °C

complex	$\Delta\nu \pm 0.3$,[a] Hz	magnetic moments $\mu_B \pm 0.05$
α-$[SiW_{12}O_{40}]^{5-}$	9.0	1.3
α-$[P_2W_{18}O_{62}]^{7-}$	10.3	1.4
α-$[P_2Mo_3W_{15}O_{62}]^{7-}$	11.0	1.5
α_1-$[P_2MoW_{17}O_{62}]^{7-}$	11.2	1.5
α_2-$[P_2MoW_{17}O_{62}]^{7-}$	12.2	1.5

[a] $\Delta\nu$ = ^{1}H NMR chemical shift difference (Hz) for *tert*-butyl alcohol's methyl protons when in 10.0 mM solutions of (1) heteropoly blue and (2) corresponding oxidized complex.

Table III. Magnetic Susceptibility Data for 2e-Reduction Products at 25 °C

complex	$\Delta\nu \pm 0.3$,[a] Hz	$\Delta\chi_M$[b] × 10^6 ± 20 × 10^6, cm^3/mol
α-$[SiW_{12}O_{40}]^{6-}$	−2.2	−180
α-$[P_2W_{18}O_{62}]^{8-}$	−1.8	−150
α-$[P_2Mo_3W_{15}O_{62}]^{8-}$	−<0.5[c]	−<40
α_1-$[P_2MoW_{17}O_{62}]^{8-}$	−1.2	−90
α_2-$[P_2MoW_{17}O_{62}]^{8-}$	−1.6	−130
α-$[P_2Mo_6W_{12}O_{62}]^{8-}$	−2.9	−230
α-$[(H_2O)ZnSiW_{11}O_{39}]^{8-}$	−1.7	−135

[a] $\Delta\nu$ = ^{1}H NMR chemical shift difference (Hz) for *tert*-butyl alcohol's methyl protons when in 10.0 mM solutions of (1) heteropoly blue and (2) corresponding oxidized complex. [b] $\Delta\chi_m$ = difference in molar magnetic susceptibilities of 2e blue and oxidized anion. [c] Not accurately measurable, but 2e peak is asymmetric, indicating a shift difference of −<0.5 Hz.

Heretofore, Evans's method measurements have been widely used to evaluate paramagnetic susceptibilities. The present adaptation enables accurate assessment of relative diamagnetisms in solution.

The modified procedure was first checked by measuring three paramagnetic heteropoly species for which magnetic moments are given in the literature. The susceptibilities of solid potassium salts of $[Co^{2+}W_{12}O_{40}]^{6-}$ and of $[Fe^{3+}W_{12}O_{40}]^{5-}$ have been measured very accurately[28,42] yielding μ_{eff}'s of 4.26 and 5.88 μ_B, respectively. The modified Evans method, using α-$[SiW_{12}O_{40}]^{4-}$ in the inner tube, gave magnetic moments of 4.28 and 5.88 μ_B, respectively. The magnetic moment for the 1e heteropoly blue α-$[SiW_{12}O_{40}]^{5-}$ was found by the modified Evans method to be 1.30 μ_B, while an earlier determination[22] by the nonspinning method (wherein the standard is not in contact with the heteropoly complex) had yielded 1.3 μ_B.

Although it has recently been suggested[43] that alcohols form complexes with heteropoly species, the same paper reported that tertiary alcohols apparently do not. Furthermore, our procedure used about a 30-fold excess of *tert*-butyl alcohol, so any rapid exchange with an alcohol–heteropoly complex would produce an entirely negligible shift.

Because the volume of solution in the outer tube is much greater than that in the inner tube, the ^{1}H NMR signal from *tert*-butyl alcohol (TBA) in the outer tube is much more intense than the signal from the same concentration of TBA in the inner tube. This allows immediate identification of which signal comes from each tube and hence the direction of the shift difference.

The results of the magnetic measurements by the modified Evans method are given in Table II for 1e blues and in Table III for 2e blues. As expected, for the usual geometry of a superconducting magnet, the 1e-reduced anions (paramagnetic) shifted the ^{1}H signal of *tert*-butyl alcohol (TBA) to higher frequencies (by 9–12 Hz) versus the TBA signal

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from the solution containing nonreduced species. On the other hand the TBA signals from the solutions containing 2e heteropoly blues (diamagnetic) *were all shifted to lower frequencies* versus the TBA signals from the solutions of the diamagnetic nonreduced complexes. Thus, the 2e-reduced species are all *more* diamagnetic than their fully oxidized heteropoly parents.

The magnitudes of these shifts for 2e species were 1-3 Hz except for the α-$[P_2Mo_3W_{15}O_{62}]^{8-}$ anion, for which the TBA peak merely acquired asymmetry, indicating a shift of <0.5 Hz.

Discussion

The results for the 2e heteropoly blues examined herein confirm that none of them is paramagnetic. In fact each is shown to be more diamagnetic than its oxidized parent. The excess diamagnetism of a 2e blue can be explained as arising from field-induced circulation of the added electrons, which generates a magnetic field opposed to the applied field (ring-current effect).

According to Langevin's equation,[44] the diamagnetic susceptibility of an atom containing n electrons is proportional to the sum of the squared values for all the electrons' average orbital radii (r_i's) (eq 3) where r_i is in centimeters and χ in centimeters

$$\chi = (-2.83 \times 10^{10}) \sum_n r_i^2 \qquad (3)$$

cubed per mole. The equation can be extended to circulating delocalized electrons in a molecule. This approach was used by Pauling,[45] who applied Langevin's equation to calculate the ring-current effect on the diamagnetism of benzene, replacing r in eq 3 by the radius of the ring-current loop.

The Langevin equation also interrelates r, the radius of the blue electron's possible loop, to the magnitude of the excess diamagnetism provided to a heteropoly blue complex by the ring current of blue electrons.

The ring current in the nearly spherical 2e heteropoly blue complex, α-$[SiW_{12}O_{40}]^{6-}$, is always free to be in a plane nearly perpendicular to the external magnetic field. The experimental excess diamagnetism for that complex is -180×10^{-6} cm^3/mol for two delocalized electrons or -90×10^{-6} cm^3/mol per electron. From this result the reported difference between the diamagnetism of W^{5+} (-19×10^{-6} cm^3/mol) and W^{6+} (-13×10^{-6} cm^3/mol) must be subtracted. This yields a total effect of -84×10^{-6} cm^3/mol per blue electron, from which the Langevin equation yields a ring-current radius of 5.4 ± 0.2 Å. The crystallographic distance from the centers of numerous Keggin ions to the *centers* of their outer oxygen atoms is 5.2 Å, while the hydrodynamic radius of α-$[SiW_{12}O_{40}]^{4-}$ has been estimated as ~5.6 Å.[46,47] This result substantiates a delocalization primarily through the outer W–O shell of the complex, in accord with evolving ^{183}W NMR data.

The total excess diamagnetism for the 2e blue α-$[P_2W_{18}O_{62}]^{8-}$ is -150×10^{-6} cm^3/mol. The blue electrons in this complex circulate only throughout its two 6W belts[7] (see Figure 1) while the blue electrons in the α-12-tungstosilicate structure are delocalized almost spherically. Although the radius of each 6W belt of the 18-tungstodiphosphate Wells–Dawson structure is essentially identical with the radius in the α-12-tungstosilicate Keggin species, the ring current in the nearly spherical Keggin ion is always free to be in a plane nearly perpendicular to the external magnetic field, whereas the anisotropy and randomness of orientation of the Wells–Dawson species reduces somewhat the effectiveness of its ring current in adding diamagnetism.

For 1e-reduced α-SiW_{12} and α-P_2W_{18} species, the ring-current effect would be expected to lower each observed paramagnetic moment by ~0.1 μ_B. Interestingly, after subtraction of this excess diamagnetism in the 1e-reduced α-P_2W_{18} anion, its remaining paramagnetic moment becomes equal to the paramagnetic moment of α_1-$[P_2MoW_{17}O_{62}]^{7-}$ anion, wherein the one added electron is localized on the more easily reduced Mo atom[7] in one of the belts, where it cannot contribute to a ring-current effect. The localization of one electron on Mo is also strongly supported by the ^{183}W NMR spectrum.[23]

As was observed previously[22] for three compounds, the paramagnetic moments of the 1e heteropoly blue tungstates are somewhat smaller than the spin-only value (1.73 μ_B) for one unpaired electron. This may be attributed to spin–orbit coupling.[22] If the addenda d^1 atoms (W^{5+} or Mo^{5+}) were at the centers of regular octahedra (i.e., having orbitally degenerate T ground states), the lowerings of the magnetic moments by such couplings would be expected to be even greater than those observed,[48] but the addenda octahedra are significantly distorted in these complexes, which vitiates the orbital degeneracy.

In α-$[P_2Mo_3W_{15}O_{62}]^{8-}$ the three Mo atoms are in one Mo_3O_{13} 3-fold cap of the complex (Figure 1), and the two added blue electrons are delocalized over those three Mo atoms only.[7] This produces a ring current of much smaller radius, and so the excess diamagnetic susceptibility of the 2e-reduction product is only -40×10^{-6} cm^3/mol of complex or less (Table III). For the magnetic moment of the 1e blue of this complex, the ring-current correction is, accordingly, much less than 0.1 μ_B. Therefore, the μ_{eff} for the 1e-reduction product is 1.5 μ_B (to two significant figures), the same as that of α_1- and α_2-$[P_2MoW_{17}O_{62}]^{7-}$ (in each of which the single added electron is mainly immobilized on Mo), and it is also the same as the value for α-$[P_2W_{18}O_{62}]^{7-}$ after correction for its ring current (see Table II).

The cap-substituted 2e blue, α_2-$[P_2MoW_{17}O_{62}]^{8-}$, has a somewhat larger ring-current contribution to diamagnetism than would be expected purely on the basis of one added electron being anchored on Mo^{5+} and the other free to circulate in the belts of the complex. The ^{183}W NMR spectrum of this complex strongly suggests, however, that the one electron that spends most of its time on the Mo^{5+} does nevertheless become sparingly delocalized into the 6W belts.[23] This is consistent with the fact that added blue electrons strongly favor residency in belts of Wells–Dawson structures.[7,18,23,29,49]

The excess diamagnetism for belt-substituted 2e-reduced α_1-$[P_2MoW_{17}O_{62}]^{8-}$ clearly indicates that one electron is localized on the Mo and the other is responsible for a one-electron ring current.

The 2e blue, α-$[P_2Mo_6W_{12}O_{62}]^{8-}$ (see Figure 1), has its added electrons delocalized over the six Mo atoms,[7] which form an elliptical loop of MoO_6 octahedra attached to each other exclusively by corner sharing. The ring-current's contribution to the diamagnetism is large (-230×10^{-6} cm^3/mol) because the average radius of the loop is large and possibly because corner sharing between MoO_6 octahedra offers less resistance to electron circulation than does edge sharing.[23,50] This interpretation is consistent with the fact that the scalar coupling constant between W's in corner-sharing WO_6 octahedra is larger than that between edge-sharing WO_6 octahedra.[6f]

The α-$[(H_2O)ZnSiW_{11}O_{39}]^{8-}$ 2e blue has a somewhat lower ring-current contribution to its diamagnetism than does the 2e-reduction product α-$[SiW_{12}O_{40}]^{6-}$ (Table III). In the former complex a Zn atom has replaced a W atom of the latter complex (Figure 1). The smaller ring-current effect is attributable to the fact that the Zn does not transmit the circulating electrons well[9] and so blocks ring currents in some of the intersecting loops. Thus, the Zn complex can have fully effective ring currents only when it is in certain orientations, when an unblocked loop is in a plane perpendicular to the magnetic field.

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The rather elegant fit of all these complexes and considerations demonstrates the reality of these ring currents, their potential value as a structural tool, and the accuracy of the Evans method, when used as described, for evaluating small differences in magnetic susceptibilities.

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Organometallic Thermochemistry. Metal Hydrocarbyl, Hydride, Halide, Carbonyl, Amide, and Alkoxide Bond Enthalpy Relationships and Their Implications in Pentamethylcyclopentadienyl and Cyclopentadienyl Complexes of Zirconium and Hafnium

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Abstract: Metal–ligand bond disruption enthalpies (D) have been determined in the series Cp'_2MX_2, Cp_2MX_2, $Cp'MX_3$ (M = Zr, Hf; $Cp' = \eta^5\text{-}Me_5C_5$; $Cp = \eta^5\text{-}C_5H_5$; M = Zr, Hf; X = hydrocarbyl, hydride, alkoxide, amide, halide) and in $Cp'_2Zr(CO)_2$ by anaerobic isoperibol batch-titration calorimetry. Heats of solution in toluene were measured followed by heats of reaction with HCl, I_2, C_6F_5OH, C_6H_5OH, CF_3CH_2OH, or t-BuOH in toluene. Derived $D(M\text{–}X)$ values decrease in the order OH $\approx$ Cl > alkoxide $\approx$ NH_2 > phenoxide > I $\approx$ H > aryl > Me > alkyl, metallacyclopentane > $\eta^1{:}\eta^5\text{-}CH_2C_5Me_4$ M–C σ bond > CO. By using $D(Cl_3M\text{–}Cl)$ as a reference point, $D(M\text{–}X)$ values are found to be rather large (e.g., for M = Zr(R): 78 (H), 73 (Ph), 67 (Me) kcal/mol) and not highly sensitive to ancillary η^5-cyclopentadienyl ligation. $D(Hf\text{–}X) - D(Zr\text{–}X)$ is estimated to be ca. 4 kcal/mol. Ancillary alkoxide ligands enhance $D(Zr\text{–}H)$ in the $Cp'_2ZrH_2/Cp'_2Zr(OR)H$ series by ca. 5 kcal/mol. The metallacycle $Cp'_2\overline{ZrCH_2(CHEt)_2CH_2}$ exhibits negligible ring strain while that in the zirconaindan $Cp'_2\overline{ZrCH_2CH_2\text{-}o\text{-}C_6H_4}$ is ca. −10 kcal/mol. A plot of $D(Zr\text{–}X)$ vs $D(H\text{–}X)$ is not linear but shows very substantial scatter. However, reasonably linear plots are observed within ligand subgroups such as hydrocarbyls, alkoxides, and halides. This behavior can be qualitatively explained on the basis of metal and ligand electronegativities. The quantities $D(M\text{–}H) - D(M\text{–}Me)$ and $D(M\text{–}I) - D(M\text{–}Me)$ vary considerably across the transition-metal series and are informative indices of metal–ligand bonding. The former is small for the present group 4 compounds and the latter large. The present data are used to semiquantitatively interpret a number of group 4 centered transformations. Among the conclusions drawn are that β-H elimination processes are usually endothermic; many C–H activating cyclometalation processes are endothermic, hence entropically driven (e.g., $Cp'_2ZrPh_2 \rightarrow Cp'Zr(Ph)(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4) + PhH$); Zr(II) → Zr(IV) oxidative additions are highly exothermic; $D(Cp'_2Zr\text{–benzyne}) \gtrsim 120$ kcal/mol; early transition metal/lanthanide/actinide $M(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)$ species are energetically poised to serve as intermediates in a number of addition and elimination processes; and the large magnitude of $D(M\text{–}OR)$ is one major driving force for the formation of alkoxide-like end products in group 4 centered CO activation chemistry.

It is becoming increasingly apparent that metal–ligand bond enthalpy data can afford invaluable insights into important reaction patterns in organometallic chemistry and catalysis.[1,2] Recent research in this laboratory has concentrated on measuring relative solution-phase homolytic bond disruption enthalpies[3] (formally defined in the gas phase for the adiabatic process shown in eq 1)

$$D(L_nM\text{–}R) = \Delta H^\circ_f(L_nM) + \Delta H^\circ_f(R^\bullet) - \Delta H^\circ_f(L_nM\text{–}R) \quad (1)$$

$$L_n = \text{ancillary ligand array}$$

in organoactinides by protonolytic (eq 2 and 3)[4] or halogenolytic

$$L_nM\text{–}R + HOR' \rightarrow L_nM\text{–}OR' + RH + \Delta H_{rx} \quad (2)$$

$$\Delta H_{rx} = D(L_nM\text{–}R) + D(H\text{–}OR') - D(L_nM\text{–}OR') - D(R\text{–}H) \quad (3)$$

(eq 4 and 5)[5] isoperibol titration calorimetry.[6] Assuming the L_nM

$$L_nM\text{–}R + X_2 \rightarrow L_nM\text{–}X + R\text{–}X + \Delta H_{rx} \quad (4)$$

$$\Delta H_{rx} = D(L_nM\text{–}R) + D(X_2) - D(L_nM\text{–}X) - D(R\text{–}X) \quad (5)$$

fragment remains structurally/energetically invariant (vide infra), *relative* $D(L_nM\text{–}R)$ parameters, "anchored" to estimated (usually from $\bar{D}$ or D_1 data for homoleptic derivatives[4]) $D(L_nM\text{–}OR')$ or $D(L_nM\text{–}X)$ values, can be obtained with high precision. Such $D(L_nM\text{–}R)$ data, while only "semiabsolute" in that they are anchored to estimated $D(L_nM\text{–}OR)/D(L_nM\text{–}X)$ data, are invaluable for understanding transformations among L_nMR/L_nMR' species.[4] In addition, it has recently been proven possible to determine *absolute* $D(L_nU\text{–}X)$ parameters via calorimetry of $L_nU/L_nUX/L_nUR$ ensembles.[5a]

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