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Effect of Alkyl Substituents on the First Ionization Potential and on $5d^{10}$ Ionization in Dialkylmercury Compounds

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Received January 22, 1976 AIC60064S

The He I photoelectron spectra of a series of dialkylmercury compounds, symmetrical (R_2Hg) as well as unsymmetrical (RHgR′), have been obtained. These compounds differ significantly from homologous series previously studied by PES in that ionization proceeds from a bonding orbital as opposed to a nonbonding orbital. Consequently, alkyl substituent effects on the first ionization potential along the series of RHgR′ (R′ = methyl, ethyl, isopropyl, *tert*-butyl) exhibit a marked "saturation" effect, in contrast to the "additive" relationship observed in the other species. The origin of this effect is discussed. In contrast, ionization of the 5d electrons, which are not involved in bonding, shows the usual additive dependence on alkyl substitution. Mercury atom charges and electronegativities of the alkyl groups are estimated, based on the shift in the 5d band in R_2Hg from Hg. The sensitivity of the ionization potential to substituent effects in the series of dialkylmercury compounds is found to decrease in the order RHgMe > RHgEt > RHg-*i*-Pr > RHg-*t*-Bu.

Introduction

The uv photoelectron spectra (PES) of some divalent compounds of the group 2B metals, including the ionization from an inner-shell d orbital, have been reported recently.[2-5] Only one of these papers[2a] deals with alkyl derivatives of mercury, and then only briefly. We have examined the PES of an extensive series of mercury dialkyls by systematically varying the structure of the alkyl group from methyl through *tert*-butyl and neopentyl, in order to probe the effect of alkyl substituents. The series of dialkylmercury compounds differs from that of other alkyl-substituted compounds examined previously, in that no high-lying nonbonding electrons are present and the first ionization potential must result from removal of electrons from bonding orbitals. The study of dialkylmercury compounds also allows a direct comparison to be made of alkyl substituent effects on the highest occupied bonding orbital (HOMO), with substituent effects on the ionization from an orbital not directly involved in bonding, viz., the mercury 5d orbitals.

Experimental Section

The photoelectron spectrometer used in these studies has been previously described.[6] The dialkylmercury compounds were prepared in pure form by the general method of Singh and Reddy,[7] and they all gave appropriate NMR, mass spectral, gas chromatographic, and elemental analyses. All of the compounds were sufficiently volatile at room temperature to be admitted directly into the ionization chamber in the gas phase. A xenon–argon mixture was used as an internal calibration standard for each spectrum.

Results and Discussion

The He I photoelectron spectra of dialkylmercury compounds show two principal bands of interest to us. The first ionization potential, occurring in a range between 7.57 eV (di-*tert*-butylmercury) and 9.33 eV (dimethylmercury) is included in a fairly broad, unsymmetrical band. A second, weaker band occurs between 14.4 and 15.0 eV and has been attributed to ionization from the mercury $5d^{10}$ shell.[2a] The ionization energies for these two bands are tabulated in Table I. Representative spectra are reproduced in Figure 1 for one series of alkyl(methyl)mercury compounds, i.e., $R–Hg–CH_3$. The internal consistency of the data is illustrated in Figure 2 by a comparison of the ionization potentials of the methylmercury alkyls with those of the ethylmercury analogues.

Table I. The First and $5d^{10}$ Vertical Ionization Potentials (eV) of Dialkylmercury Compounds

Compd	1st IP	$5d^{10}$ IP	Compd	1st IP	$5d^{10}$ IP
$(CH_3)_2Hg$	9.33	14.93	$(i\text{-}C_3H_7)_2Hg$	8.03	14.46
$(CH_3)(C_2H_5)Hg$	8.84	14.85	$(C_2H_5)(t\text{-}C_4H_9)Hg$	8.06	*a*
$(C_2H_5)_2Hg$	8.45	14.71	$(i\text{-}C_3H_7)(t\text{-}C_4H_9)Hg$	7.73	*a*
$(CH_3)(i\text{-}C_3H_7)Hg$	8.48	14.86	$(n\text{-}C_4H_9)_2Hg$	8.35	*a*
$(CH_3)(i\text{-}C_4H_9)Hg$	8.75	14.74	$(i\text{-}C_4H_9)_2Hg$	8.30	14.47
$(CH_3)(t\text{-}C_4H_9)Hg$	8.31	*a*	$(t\text{-}C_4H_9)_2Hg$	7.57	*a*
$(C_2H_5)(i\text{-}C_3H_7)Hg$	8.18	14.61	$(i\text{-}C_4H_9)(neo\text{-}C_5H_{11})Hg$	8.33	14.49
$(n\text{-}C_3H_7)_2Hg$	8.29	14.63	$(neo\text{-}C_5H_{11})_2Hg$	8.30	14.41

[a] The intensity of this band was too low to observe it above the noise level of the spectrum.

The effect of alkyl substitution on the first ionization potential of a series of alkyl derivatives is attributed primarily to polarization effects in the molecular ion final state.[8,9] It has been recognized that such electronic effects are additive along the series Me, Et, *i*-Pr, and *t*-Bu.[10] Thus the energy effect of replacing Me by Et is expected to equal that of replacing Et by *i*-Pr or of replacing *i*-Pr by *t*-Bu. In each case, α hydrogens in CH_3 are being sequentially replaced by methyl groups. Such a relationship is observed in chemical equilibria and reaction rates,[10] as well as in ionization potentials determined by PES.[11,12]

A recent relevant example of this additivity relationship involves the proton affinities (PA) of alcohols which were found to increase by increments of 6 ± 1 eV along this series.[13] The equal increments in proton affinities, Δ(PA), are particularly noteworthy, since Martin and Shirley have shown[9] that the variation in proton affinities of this series of alcohols should be equal to the variation in the O(1s) binding energy of the same compounds. Indeed a plot of the proton affinities of alcohols against their ionization potentials is linear with a unit slope. This correlation suggests that both effects arise from the polarization of the alkyl group in response to a unit positive charge on oxygen.

Such additive energy effects have been used by Taft[10] as a criterion for identifying polar effects as denoted by the empirical substituent constant σ^* (Me:Et:*i*-Pr:*t*-Br =

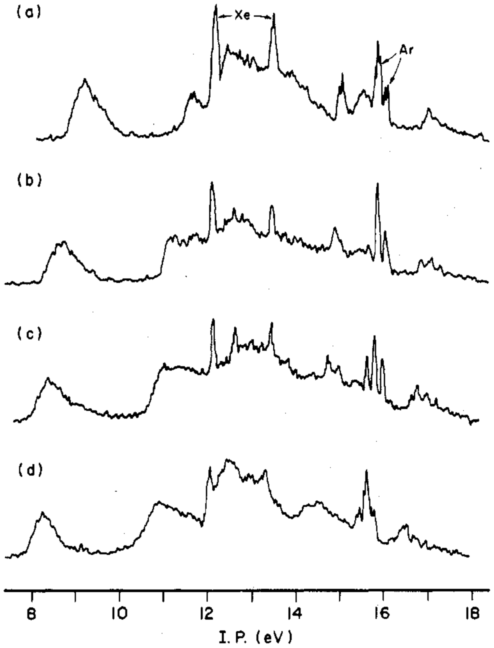


Figure 1. He I photoelectron spectra of the series RCH_3Hg: (a) R = CH_3; (b) R = C_2H_5; (c) R = i-C_3H_7; (d) R = t-C_4H_9. The bands due to the Xe-Ar calibration mixture occurring in each spectrum are indicated in (a).

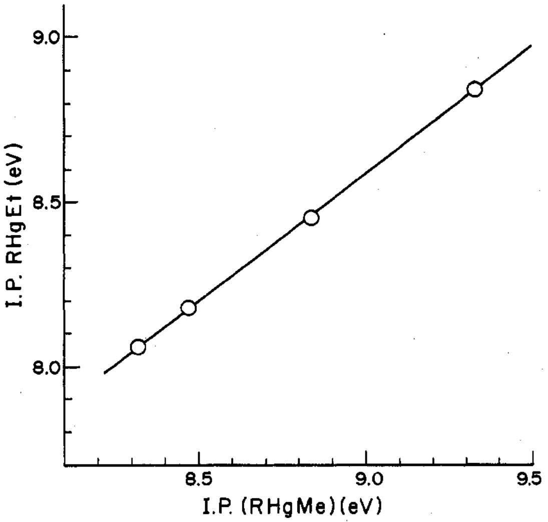


Figure 2. First ionization potential of RC_2H_5Hg vs. the first ionization potential of RCH_3Hg.

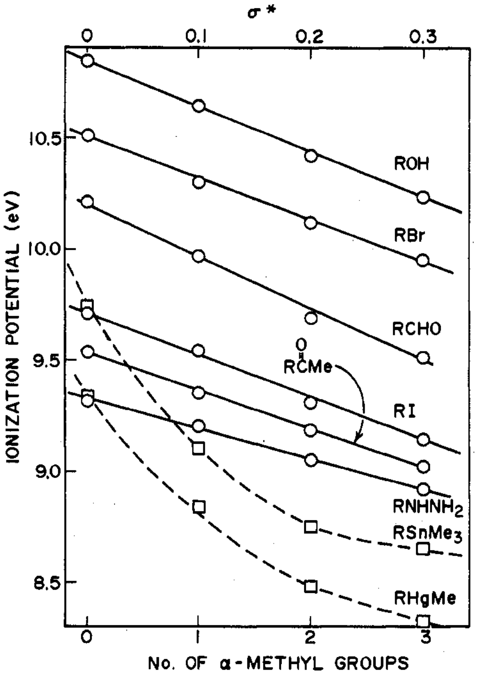


Figure 3. First ionization potential of alkyl-substituted compounds vs. σ* (see text) and the number of α-methyl groups. Sources: ROH, ref 11; RBr, ref 14; RCHO, ref 12; RI, ref 12; $RCOCH_3$, ref 12; $RNHNH_2$, ref 15; $RSn(CH_3)_3$, ref 17.

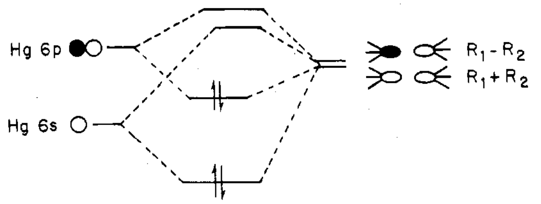
0:0.10:0.19:0.30). It has been shown that the Taft relationship holds for the ionization potentials of alcohols[11] and other alkyl compounds.[12] Figure 3 illustrates the linear relationship between σ* values and the ionization potentials of a series of alcohols,[11] alkyl bromides,[14] alkylhydrazines,[15] and aldehydes.[12]

The correlation of the ionization potentials of a series of alkylmercurials, R–$HgCH_3$, also plotted in Figure 3 is distinctly *nonlinear.* The incremental changes in energies become progressively smaller or "saturated" as one proceeds from methyl to *tert*-butyl. Moreover, the same pattern of saturation obtains for the analogous series of Grignard reagents R–MgX[16] and trimethyltin compounds $RSnMe_3$[17] measured independently.

The reason for the difference between energy effects which are *saturated* and those that are *additive* is not completely clear. The ionization potentials of dialkylmercury compounds are not simply related to the size of the alkyl group since the first ionization potentials of di-*n*-propyl-, diisobutyl-, and dineopentylmercury are the same within 0.01 eV. The latter also indicates that the effect due to substitution of methyl groups in the β position of the alkyl chain is highly attenuated relative to that accompanying α substitution.

There does, however, appear to be a relationship between the difference in behavior in each series and the nature of the highest occupied molecular orbital (HOMO). For those systems containing nonbonding electrons, the ionization proceeds from a HOMO which is largely orthogonal to the σ-bonding orbitals, particularly those associated with the bonding of the heteroatom to carbon. Thus, although interactions between the alkyl group and the heteroatom can be observed,[14] ionization from the HOMO is only weakly coupled to the bonding system and additivity is observed.

In contrast, the ionization process in organometals such as Me_2Hg proceeds from a molecular orbital that has substantial metal–carbon bonding character. This conclusion[18] may be portrayed with a simple LCBO diagram[19] as



where the HOMO is formed from the bonding combination of the antisymmetric combination of the σ-type group orbitals of the alkyl fragments with the mercury 6p atomic orbital. That this interaction is significant receives support both from theory[18] and from other photoelectron spectroscopic studies.[2a] In fact, we suggest that ionization of the HOMO of alkyl radicals [i.e., R → R^+ + e^-] should serve as a reasonable model for the ionization of the HOMO of organomercurials. Significantly, both the measured ionization potentials of alkyl radicals[20] and those obtained from SCF–MO calculations[21] show the characteristic saturation effect described above, and they correlate well with the ionization potentials of organomercurials examined in this study (Table II). Thus, in this

Table II. Experimental and Calculated Ionization Potentials of Alkyl Radicals

R·	IP, eV	
	Exptl[a]	Calcd[b]
Methyl	9.84	9.95
Ethyl	8.38	8.56
Isopropyl	7.55	7.60
tert-Butyl	6.93	6.83

[a] From ref 20. [b] Using the pseudoheteroatom model for the metal group in ref 21.

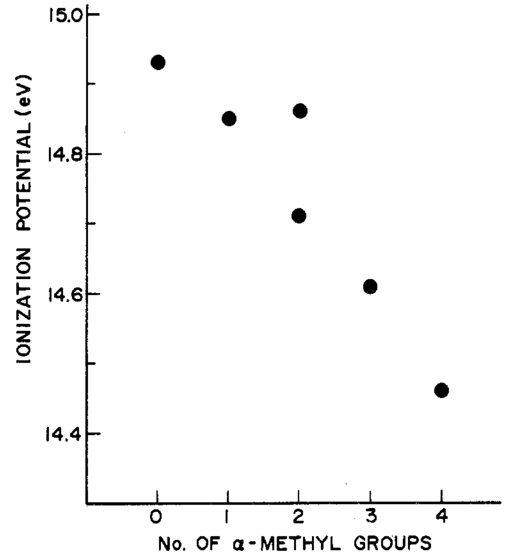


Figure 4. Ionization potential of the sharp Hg $5d^{10}$ band vs. the number of α-methyl groups.

case, ionization from the HOMO is strongly coupled to the bonding system. In such a situation, changes in electron repulsion may well be large and not effectively constant as the alkyl group is systematically varied from Me to *t*-Bu.[21] In any event, it does seem clear that in these cases saturation is observed.

It is interesting to note that a plot of the first vertical IP for the series of alkylmercurials MeHgR against the ^{199}Hg–CH$_3$ proton NMR coupling constant in the same species reveals a linear relationship. Mercury proton spin–spin coupling is generally conceded to occur via a Fermi contact mechanism,[22] and it reflects the effective nuclear charge (Z_{eff}) in the ground state. The linearity of this plot indicates that inductive electron release by the various alkyl groups in response to the constant electron demand of the methyl group in the ground state parallels electron release by the same groups in response to a constant (unit) positive charge in the molecular ion.

The rationale for the saturation effect observed for ionization of the HOMO suggests that the 5d ionization energy of mercury should show additive behavior as the 5d level has little if any involvement in bonding. In fact, as shown in Figure 4, the 5d ionization energy does decrease linearly with the number of α-methyl groups in the alkyl substituent. Note that the 5d ionization energy for $(CH_3)_2Hg$ is greater than that for Hg. This is opposite to what is expected if final-state effects were dominant. Ground-state (inductive) effects may be more important than final-state (polarization) effects in this case. The variation in the 5d ionization potential through the series of dialkylmercury compounds would then arise primarily from changes in the ground-state charge on the mercury atom.

Thus, the IP$_{5d}$ data can be used to calculate the charge on the mercury atom. We use the method of Siegbahn and co-workers,[23,24] which has been outlined in detail for mercury(II) compounds by Eland.[2a] The calculated charges are presented in Table III.

Table III. Calculated Charges (q) on the Mercury Atom and Approximate Electronegativities of the Alkyl Groups[a]

Compd	q	Electronegativity
$(CH_3)_2Hg$	0.0234+	1.98 (CH_3)
$(CH_3)(C_2H_5)Hg$	0.000	
$(C_2H_5)_2Hg$	0.0338–	1.81 (C_2H_5)
$(CH_3)(i\text{-}C_3H_7)Hg$	0.000	
$(CH_3)(i\text{-}C_4H_9)Hg$	0.0260–	
$(C_2H_5)(i\text{-}C_3H_7)Hg$	0.0599–	
$(n\text{-}C_3H_7)_2Hg$	0.0547–	1.75 ($n\text{-}C_3H_7$)
$(i\text{-}C_3H_7)_2Hg$	0.0990–	1.62 ($i\text{-}C_3H_7$)
$(i\text{-}C_4H_9)_2Hg$	0.0703–	1.70 ($i\text{-}C_4H_9$)
$(i\text{-}C_4H_9)(neo\text{-}C_5H_{11})Hg$	0.0911–	
$(neo\text{-}C_5H_{11})_2Hg$	0.112–	1.58 ($neo\text{-}C_5H_{11}$)

[a] The $5d^{10}$ ionization bands for the compounds $(CH_3)(t\text{-}C_4H_9)Hg$, $(C_2H_5)(t\text{-}C_4H_9)Hg$, $(i\text{-}C_3H_7)(t\text{-}C_4H_9)Hg$, $(n\text{-}C_4H_9)_2Hg$, and $(t\text{-}C_4H_9)_2Hg$ were not observed, so charges and electronegativities could not be calculated.

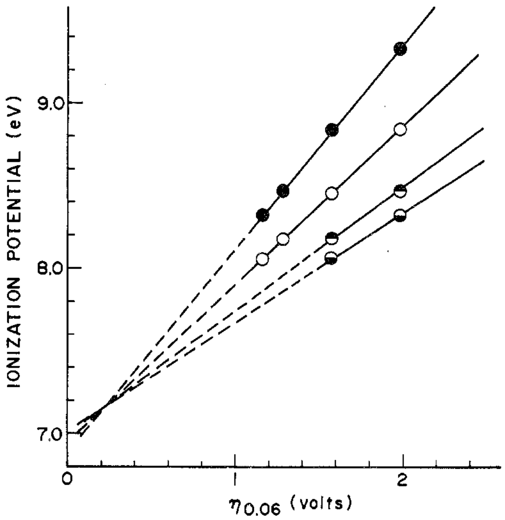


Figure 5. First ionization potential of RHgR′ vs. the solution oxidation potential of RMgBr. The slopes represent the sensitivities of the first ionization potentials of RHgR′ to alkyl substitution: ●, R′HgMe; ○, R′HgEt; ⊖, R′Hg-*i*-Pr; ◒, R′Hg-*t*-Bu.

Since the mercury atom is bonded to two alkyl groups, we can estimate that the charge produced on mercury is divided equally between the alkyl groups in the symmetrical compounds. The percent ionic character (P) in the Hg–C bond is then $(q/2) \times 100$. The electronegativities of the alkyl groups can now be calculated by using the relationship[25]

$$P = 16|\chi_A - \chi_B| + 3.5|\chi_A - \chi_B|^2 \qquad (1)$$

where χ_A and χ_B are the electronegativities of the two atoms making up the chemical bond. Taking the electronegativity of Hg to be 1.91,[4] the values in Table III are obtained. These values are noteworthy in that a sizable effort, notably by Kharasch[26] as well as by others,[27] has been directed toward the use of organomercurials to obtain an electronegativity series for alkyl groups. To our knowledge, our result is the first instance in which such electronegativities have been determined numerically. It must be pointed out, however, that the first 5d band in the spectra of several compounds is quite weak and its IP cannot be measured with a high degree of accuracy. Therefore, calculated charges and electronegativities of the alkyl groups must be regarded as having more qualitative rather than quantitative significance at this point. Nevertheless the approximately equal changes in electronegativity on proceeding from methyl to ethyl (1.98 to 1.81) and from ethyl to isopropyl (1.81 to 1.62) are at least consistent with the additivity cited above. Furthermore, the results are in good agreement with the qualitative trend in electronegativities reported earlier.[26,27]

A final point of interest relates to the sensitivity of the various series of mercurials, RHgR′, to alkyl substitution. In Figure 5, the ionization potentials of a series of dialkylmercury compounds R–Hg–R′ have been plotted against the oxidation potentials of the corresponding Grignard reagent (representing a common scale). The slopes decrease in the order R′HgMe > R′HgEt > R′Hg-*i*-Pr > R′Hg-*t*-Bu. We attribute this result to the fact that partial delocalization of charge by the first R group in the molecular ion diminishes the effect of the second group R′; or, stated alternatively, there is less charge remaining to be delocalized. The apparent intercept at about 7.2 eV (disregarding the experimental scatter in the highly substituted compounds) represents a limiting example, in which one group, extremely effective at delocalizing charge, completely nullifies the effect of the second group.

Acknowledgment. The support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. $(CH_3)_2Hg$, 593-74-8; $(CH_3)(C_2H_5)Hg$, 29138-86-1; $(C_2H_5)_2Hg$, 627-44-1; $(CH_3)(i\text{-}C_3H_7)Hg$, 29138-88-3; $(CH_3)(i\text{-}C_4H_9)Hg$, 59643-44-6; $(CH_3)(t\text{-}C_4H_9)Hg$, 59049-78-4; $(C_2H_5)(i\text{-}C_3H_7)Hg$, 59049-79-5; $(n\text{-}C_3H_7)_2Hg$, 628-85-3; $(i\text{-}C_3H_7)_2Hg$, 1071-39-2; $(C_2H_5)(t\text{-}C_4H_9)Hg$, 59049-80-8; $(i\text{-}C_3H_7)(t\text{-}C_4H_9)Hg$, 59049-81-9; $(n\text{-}C_4H_9)_2Hg$, 629-35-6; $(i\text{-}C_4H_9)_2Hg$, 24470-76-6; $(t\text{-}C_4H_9)_2Hg$, 23587-90-8; $(i\text{-}C_4H_9)(neo\text{-}C_5H_{11})Hg$, 59643-45-7; $(neo\text{-}C_5H_{11})_2Hg$, 10284-49-8.

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Low-Temperature Electron Spin Resonance Spectra of Heteropoly Blues Derived from Some 1:12 and 2:18 Molybdates and Tungstates

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Received March 22, 1976 AIC60215R

X-Band ESR spectra of nine reduced heteropoly anions (heteropoly blues) have been recorded at temperatures between 4.2 K and room temperature. The spectrum of $PMo^{V}Mo_{11}O_{40}{}^{4-}$ is isotropic ($g = 1.945$) at all temperatures and exhibits hyperfine structure (six lines) below 64 K, with $\langle a \rangle = 55 \times 10^{-4}$ cm^{-1}. The intensity of the hyperfine spectrum relative to the central (nonmagnetic) line increases as the temperature is lowered. The spectra of five reduced 1:12 tungstates are rhombic at low temperatures, with $g_1 = 1.848$–1.852, $g_2 = 1.805$–1.827, and $g_3 = 1.759$–1.79. Above 50–80 K, depending on the anion, the spectra appear isotropic[1] due to line broadening. The spectra of reduced α-$P_2W_{18}O_{62}{}^{6-}$ and α-$As_2W_{18}O_{62}{}^{6-}$ remain rhombic at higher temperatures, with $g_1 = 1.905$, $g_2 = 1.85$, and $g_3 = 1.81$. The spectrum of the reduced β isomer of $P_2W_{18}O_{62}{}^{6-}$ is isotropic ($g = 1.852$) at all temperatures down to 13 K. All of the ESR spectra are discussed in terms of weakly trapped Mo(V) or W(V) valences. The rate of intraionic electron delocalization in $PMo^{V}Mo_{11}O_{40}{}^{4-}$ at 6 K must be greater than ca. 10^8 s^{-1} implying a much lower activation energy than predicted by the Hush model for mixed valence compounds. The source of the rhombic crystal field for tungsten atoms in the 1:12 (Keggin) structure is discussed and the major differences between the spectra of 1:12 and 2:18 anions are rationalized. Two-electron heteropoly blues appear diamagnetic, probably through antiferromagnetic coupling of electrons localized on adjacent metal atoms.

Introduction

Heteropoly and isopoly oxo anions of vanadium, molybdenum, or tungsten are reducible to mixed-valence heteropoly "blue" isomorphs if they have structures in which the metal atoms are each bound to one, as opposed to two, *terminal* oxygen atoms.[2]. Although there are several such (type I) structures known for polyanions, most studies of heteropoly blues have been made on anions with the 1:12, $XZ_{12}O_{40}$ (Keggin), and 2:18, $X_2Z_{18}O_{62}$, structures. Optical spectra of reduced "mixed" anions, e.g., $PV^{IV}W_{11}O_{40}{}^{5-}$ and $PMo^{V}W_{11}O_{40}{}^{4-}$, are similar to those of "real" heteropoly blues, $PW^{V,VI}{}_{12}O_{40}{}^{4-}$, etc., yet according to ESR spectroscopy the valences are trapped as indicated by the above formulas.[3-5] There have been relatively few attempts to record ESR spectra of heteropoly blues, and the results have not been very conclusive. A few years ago we reported spectra for a number of reduced 1:12 and 2:18 tungstates at temperatures down to 77 K.[6] The spectra for the 1:12 anions were isotropic at 77