groups are not equivalent to one another. To further elucidate this problem, we are currently investigating the crystal and molecular structure of the complex Pd(diphos)$(N_3)_2$.

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Electron Spin Resonance in Molybdenum(V) and Tungsten(V) Compounds

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Continuing work in our laboratories has involved the preparation and characterization of transition metal alkoxides.[1-8] Particular emphasis has been placed on d^1 systems whose paramagnetism has subsequently led to the prediction of bonding properties.[7,9] For example, evidence points to more covalency in the b_2 and b_1 molecular orbitals whereas the e molecular orbital becomes more ionic from $^-OCH_3$ to $^-OC_4H_9$ in $V(OR)Cl_5^{2-}$.[7]

Other workers,[10-13] including our group,[14] have studied the effect of changing F^- to Cl^- to Br^- in $MoOX_5^{2-}$. A substantial change was found for the $g_\parallel$ value. The $g_\perp$ values also changed, but less drastically.

As yet, no study has involved the selective change of ligands on the C_{4v} axis of symmetry. Our purpose is to illustrate the g-value variation between $W(OR)Cl_5^-$ and $W(OR)_2Cl_4^-$. We will also compare magnetic tensor values for $Mo(OR)_2Cl_4^-$, $MoOCl_4^-$, and $MoOCl_5^{2-}$.

Experimental Section

Compounds.—Molybdenum(V) and tungsten(V) complexes were described previously.[5,8]

Spectroscopic Measurements.—X-Band esr spectra were recorded at 298 and 78°K on a Varian V-4502-04 spectrophotometer. First-derivative absorptions were recorded on an X-Y recorder with the X axis proportional to the magnetic field strength. A Hall probe was used as field sensor. Markings, which were placed on the recorded spectra by means of a Hewlett-Packard 524-C frequency counter, allowed calibration of the magnetic field. This data enabled calculation of hyperfine splittings. The g values were calculated from the measured magnetic field and klystron frequency.

In conversion of hyperfine values from gauss into reciprocal centimeters, the experimental g values were used in the equation $\nu = g\beta H/h$.

Results and Discussion

The spin Hamiltonian which accounts for an electron spin resonance spectrum of a compound with axial symmetry in a frozen solution is

$$H = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y)$$

where $S = {}^1/_2$, $I(^{95}Mo,\ 15.8\%;\ ^{97}Mo,\ 9.6\%) = {}^5/_2$, and $I(^{183}W,\ 14.2\%) = {}^1/_2$.

At room temperature the anisotropies add to zero and the Hamiltonian becomes

$$H = \langle g\rangle \beta H \cdot S + \langle a\rangle I \cdot S$$

$$\langle g\rangle = {}^1/_3(g_\parallel + g_\perp)$$

$$\langle a\rangle = {}^1/_3(A + 2B)$$

The high-field approximation cannot be applied rigorously because hyperfine splittings are 50 G or more in width. The eigenvalues which lead to a second-order perturbation correction of $h\nu = g\beta H_0$ are: for isotropic g

$$H_0 = H_m + \langle a\rangle m_I + \langle a\rangle^2[I(I + 1) - m_I^2]/2H_m$$

for $g_\parallel$

$$H_0 = H_m + Am_I + B^2[I(I + 1) - m_I^2]/2H_m$$

for $g_\perp$

$$H_0 = H_m + Bm_I + (A^2 + B^2)[I(I + 1) - m_I^2]/4H_m$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I. In previous equations ν is the klystron frequency and A and B are the nuclear hyperfine splitting constants. These corrections were reiterative, were performed with a program designed for this purpose,[15] and were carried out on the MSU control data 3600 computer. Five iterations were carried through. The program also contained a plot routine. The simulated spectrum was then changed by altering the magnetic tensor values until a match was obtained between the computed and experimental spectra.

Electron spin resonance spectra were obtained on powdered samples and on various solutions at 78 and 297°K. The ^{95}Mo–^{97}Mo hyperfine spectrum was observed.

An absorption in an experimental spectrum of tungsten was thought to be hyperfine structure from ^{183}W. Since no hyperfine structure could be duplicated by the computer, the absorption may have been due to a rhombic distortion or an impurity. The ^{183}W hyperfine structure is thought to be masked by the broad absorption of the isotopes with $I = 0$ becuase the half-width is approximately 100 G.

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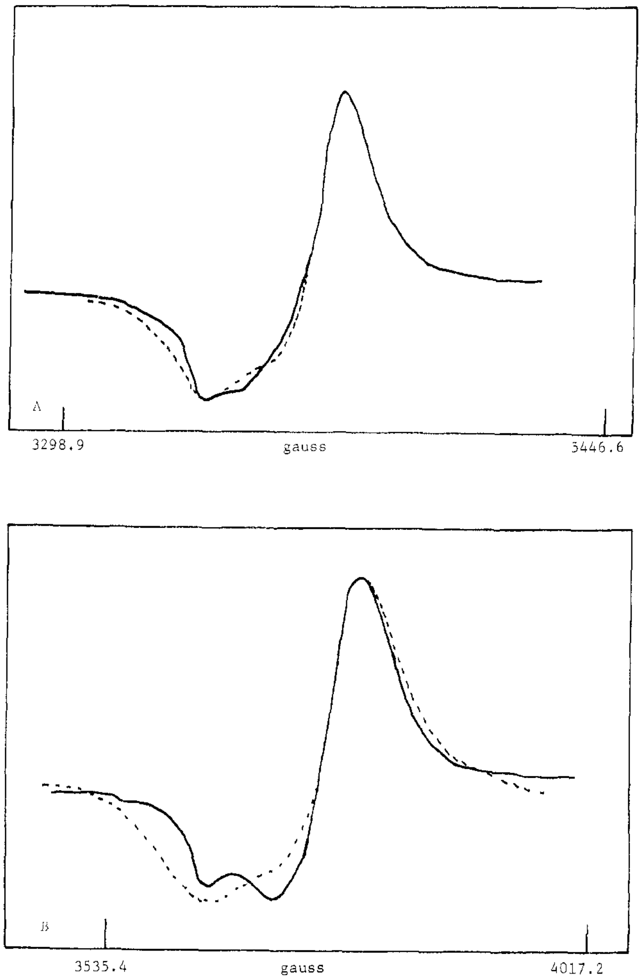

Figure 1.—Electron spin resonance spectra in CH_3NO_2 at 78°K of (A) $[(C_2H_5)_4][W(i\text{-}OC_3H_7)Cl]$ and (B) $[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$: ——, experimental; - - - - - - - -, computed.

From the bulk magnetic susceptibility data,[5] a large difference in g values was anticipated between $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$ ($\mu_{\text{eff}} = 1.36$ BM) and $[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$ ($\mu_{\text{eff}} = 1.53$ BM). Figure 1 illustrates the spectra and Table I lists the g values for mono and dialkoxo complexes of tungsten(V). The $g_\perp$ value is found to change more than $g_{\parallel}$. However, changing from Cl^- to Br^- in $[(C_2H_5)_4N][W(OCH_3)_2X_4]$ caused a greater alteration in the $g_{\parallel}$ value than $g_\perp$. A similar observation is reported[12] in complexes of the type WOX_5^{2-}. Thus in compounds of C_{4v} symmetry, it seems that axial ligands cause the greatest change in $g_\perp$ whereas equatorial ligands alter the $g_{\parallel}$ value to the greatest extent.

Further evidence for this phenomenon is obtained from a comparison of molybdenum(V) complexes. Table II contains measured magnetic tensor values. The value $g_{\parallel}$ is nearly the same for $MoOCl_4^-$, $MoOCl_5^{2-}$, and $(OCH_3)_2Cl_4^-$ and $g_\perp$ values are quite similar[12] for $MoOCl_4^-$ and $MoOCl_5^-$. However, $g_\perp$ values are lower for $Mo(OCH_3)_2Cl_4^-$ species.

TABLE I

MAGNETIC TENSOR VALUES FOR TUNGSTEN(V) COMPLEXES

Compound	Temp, °K	$\langle g \rangle$	$g_{\parallel}$	$g_\perp$
$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$				
CH_3NO_2 soln	297	1.80		
	78		1.94	1.79
Powder	297		1.85	1.75
$[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$				
CH_3NO_2 soln	297	1.74		
	78		1.79	1.72
CH_2Cl_2 soln	297	1.73		
Powder	297	1.76		
$[(CH_3)_4N][W(OC_2H_5)_2Cl_4]$				
CH_3NO_2 soln	78	(1.75)	1.80	1.73
Powder	297	1.74		
$[(CH_3)_4N][W(OCH_3)_2Cl_4]$				
CH_3NO_2 soln	78	(1.75)	1.80	1.73
Powder	297	1.74		
$[(C_2H_5)_4N][W(OCH_3)Cl_5]$				
CH_3NO_2 soln	78	(1.56)	1.70	1.49
$[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$				
CH_3NO_2 soln	78	(1.57)	1.71	1.50
$[(C_2H_5)_4N][W(n\text{-}OC_3H_7)Cl_5]$				
CH_3NO_2 soln	78	(1.58)	1.71	1.51
$[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$				
CH_3NO_2 soln	78	(1.57)	1.70	1.50
$[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$				
CH_3NO_2 soln	78	(1.57)	1.70	1.50

In an attempted ligand-exchange experiment between $Mo(OC_2H_5)_2Cl_4^-$ and SCN^-, the g values essentially remained constant and probably indicated that little exchange of either ethoxide or chloride took place with SCN^-.

If $MoOCl_4^-$ is dissolved in methanol, the spectrum changes with time. Two lines were obtained as illustrated in Figure 2A: $g = 1.943$ corresponds to $MoOCl_4^-$. Figure 2B shows the spectrum of $Mo(OC_2H_5)_2Cl_4^-$ in ethanol: $g = 1.935$ corresponds to $Mo(OCH_3)_2Cl_4^-$. Again two species are present. Since molybdenum(V) compounds are very susceptible to oxygen abstraction[16] and Funk, *et al.*,[17-19] found that oxymethoxy compounds could be isolated from methanol, the species present (in addition to parent compounds) are probably mixed alkoxo–oxo complexes.

It is also interesting to note $\langle g \rangle$ values for $MoOCl_4^-$ in methylene chloride and nitromethane. $\langle g \rangle$ is 1.956 in CH_2Cl_2 and 1.949 in CH_3NO_2. Electronic absorptions[20] attributed to the $B_2 \rightarrow E$ are to 14,600 and 13,600 cm^{-1}.[8] Thus, the larger difference between the ground and excited state, the less spin–orbit coupling occurs, and the greater is the g value.

Most powder samples gave a one-line esr absorption spectrum except $[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$ and $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$ in whose spectra $g_{\parallel}$ and $g_\perp$ could be resolved. Electron spin resonance spectra of pentachloroalkoxotungstate(V) could not be obtained in solution at room temperature. These compounds were isolated at 78° and powder esr spectra were readily obtained at room temperature. A spectrum which is believed to be that of $WOCl_4^-$, the

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TABLE II

MAGNETIC TENSOR VALUES FOR MOLYBDENUM(V) COMPLEXES

Compound	Temp, °K	$\langle g \rangle$	$g_{\|}$	$g_{\perp}$	$10^4\langle a \rangle$, cm^{-1}	10^4A, cm^{-1}	10^4B, cm^{-1}
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$							
CH_3NO_2 soln	297	1.939			43.3		
	78		1.970	1.923		70.8	31.0
CH_3OH–HCl soln	297	1.938			43.5		
	78		1.971	1.923		70.9	29.2
Powder	297		1.970	1.920			
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$							
CH_3NO_2 soln	297	1.939			43.2		
	78		1.970	1.923		71.7	28.7
C_2H_5OH–HCl soln	297	1.939					
	78		1.975	1.923		77.5	31.0
Powder	297	1.944					
CH_3NO_2–satd NH_4SCN soln	78		1.970	1.923		71.7	28.3
$[(C_3H_7)_4N](MoOCl_4)$							
CH_3NO_2 soln	297	1.949			47.1		
	78		1.970	1.934		74.7	36.1
Powder	297	1.951					
$[(C_4H_9)_4N](MoOCl_4)$							
CH_3NO_2 soln	297	1.949			46.1		
	78		1.968	1.930		75.5	36.9
CH_2Cl_2 soln	297	1.956			47.1		
Powder	297	1.949					
$[NH_4]_2[MoOCl_5]$[13]							
Powder	297	1.948	1.964	1.940			
In single crystal of $[NH_4]_2[InCl_5] \cdot H_2O$		1.948	1.9632	1.940	46.6	74.7	32.6

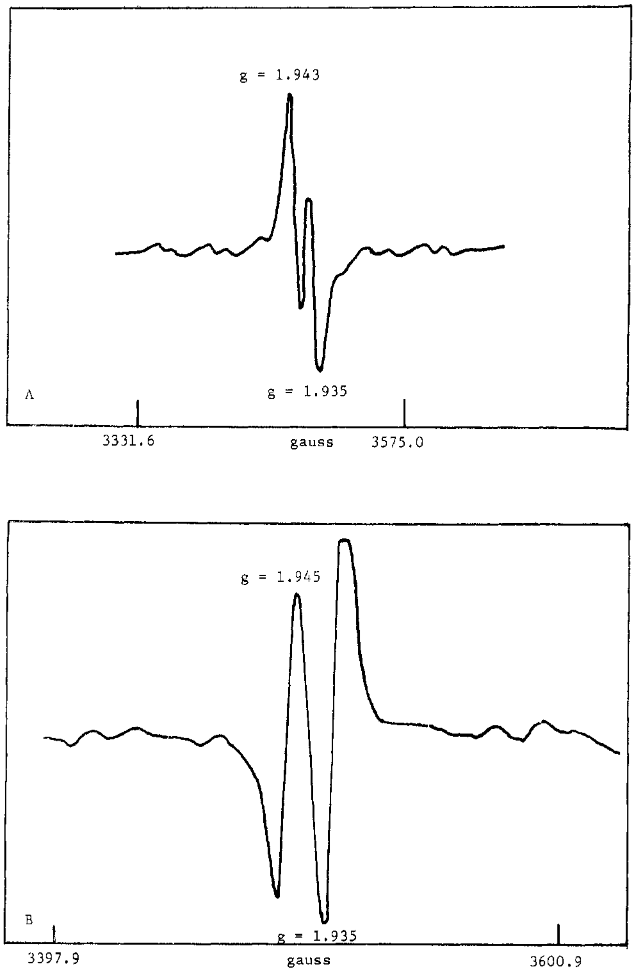

Figure 2.—Electron spin resonance spectra of (A) $[(C_3H_7)_4N](MoOCl_4)$ in CH_3OH and (B) $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$ in C_2H_5OH.

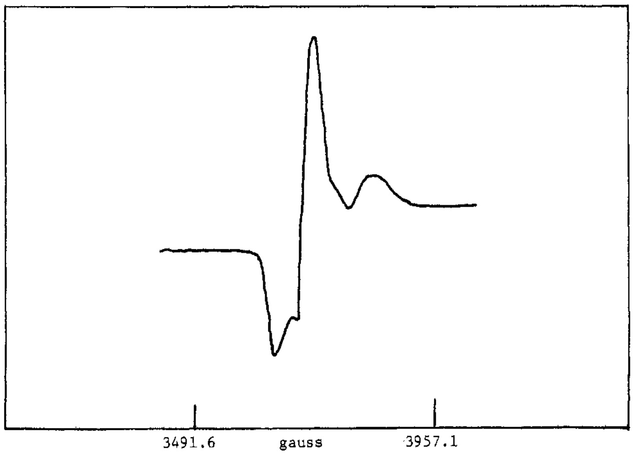

Figure 3.—Electron spin resonance spectrum of $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$ at 78°K.

decomposition product[5,8] of $W(OC_2H_5)Cl_5^-$, is observed at 78°K. The broad hump in the spectrum in Figure 3 probably arises from $W(OC_2H_5)Cl_5^-$. The g values of the presumed $WOCl_4^-$ absorption are $g_{\|}$ and $g_{\perp}$ equal to 1.80 and 1.77, respectively. These compare well[12] to those g values of $WOCl_5^{2-}$.

The powdered complex $[(C_2H_5)_4N](WCl_6)$ gave a one-line absorption spectrum at room temperature with $g = 1.79$. One line was also observed for $[(C_2H_5)_2N](WCl_6)$ doped into $[(C_2H_5)_4N](TaCl_6)$, but the author[21] only reported that the g value was less than 2. Dowsing and Gibson[22] reported that $[(C_2H_5)_4N](MoCl_6)$ gave a room-temperature spectrum with $g_{\|} = 1.977$ and $g_{\perp} = 1.935$. Distortion of the lattice is

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believed to remove the degeneracy of the ground state and an esr signal is then observed in these hexachloro complexes.[22]

Certain values of theoretical interest can be calculated for molybdenum(V) compounds if it is assumed that the d^1 electron is in the $b_2(d_{xy})$ orbital.[23]

The values of K, χ, β^2, and P_{complex} $(=\beta^2 P_{\text{ion}})$ are listed in Table III. K and χ are the isotopic contact term in reciprocal centimeters and atomic units, respectively, and β^2 is the molecular orbital coefficient for the b_2 orbital. The β^2 values indicate that the electron is a b_2 electron and spends more time in the d_{xy} orbital in dialkoxo than oxo complexes. The other values, $-K$, $-\chi$, and $\beta^2 P$, are comparable to those obtained for other molybdenum(V) complexes.[10,12,23]

TABLE III

ISOTOPIC CONTACT TERMS, K AND χ, β^2, AND P FOR MOLYBDENUM(V) COMPLEXES IN GLASSES AT 78°K

Compound	$10^4(-K)$, cm^{-1}	$10^4(-\chi)$, cm^{-1}	$10^4 P$, cm^{-1}	β^2
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	39.6	5.07	48.5	0.881
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	39.5	5.05	49.9	0.908
$[(C_3H_7)_4N](MoOCl_4)$	45.9	5.87	44.6	0.810
$[(C_4H_9)_4N](MoOCl_4)$	46.5	5.95	44.5	0.809

In the cases of the tetraethylammonium salts of the tetrachlorodimethoxomolybdate(V) and the tetrachlorodiethoxomolybdate(V) ions in solutions in the appropriate alcohols, which had been saturated with HCl, the experimental g and A values could be used to calculate the molecular orbital coefficients $N_{\pi 1}$, $N_{\pi 2}$, and $N_{\sigma 2}$ in the equations

$$|B_2\rangle^* = N_{\pi 2}\,(\mathrm{d}_{xy} - \lambda_{\pi 2}\phi_{\mathrm{b2}})$$

$$|B_1\rangle^* = N_{\sigma 2}(\mathrm{d}_{x^2-y^2} - \lambda_{\sigma 2}\phi_{\mathrm{b1}})$$

$$|E\rangle^* = N_{\pi 1}[\mathrm{d}_{xz}(\text{or } \mathrm{d}_{yz}) - \lambda^{\mathrm{e}}{}_{\pi 1}\phi^{\mathrm{e}}{}_{\mathrm{e}} - \lambda^{\mathrm{a}}{}_{\pi 1}\phi^{\mathrm{a}}{}_{\mathrm{e}}]$$

These calculations were carried out exactly as in our work with the monoalkoxo complexes of vanadium(IV)[7] and in the work of Manoharan and Rogers[13] on molybdenyl–halo complexes. In the cases of the tungsten(V) compounds anisotropic A values could not be determined well enough to permit such calculations.

For the methoxo complex we took the following values as those of molybdenyl complexes: $S_{\mathrm{b2}} = 0.12$, $S_{\mathrm{b1}} = 0.16$, $S_{\mathrm{e}} = 0.20$, $\xi_{\text{metal}} = 820\ \text{cm}^{-1}$, $\xi_{\text{ligand}} = 587\ \text{cm}^{-1}$, and $P = 55.0$. The energies of the $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions[8] are 11.7 and $21.8 \times 10^3\ \text{cm}^{-1}$, respectively. In the case of the ethoxo complex the same "molybdenyl values" were used for the overlap integrals, spin–orbit coupling constants, and "P," and the transition energies were taken from spectra[8] and equaled 12.1 and $21.5 \times 10^3\ \text{cm}^{-1}$.

In the methoxo case $N_{\pi 1} = 0.968$, $N_{\pi 2} = 0.939$, $N_{\sigma 2} = 0.864$, and the spin density in the equatorial $3p_\pi$ orbital is 4.3%. For the ethoxo complex we found $N_{\pi 1} = 0.947$, $N_{\pi 2} = 0.967$, $N_{\sigma 2} = 0.811$, and a spin density of 2.8%.

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The Structure of Bis(2,4-pentanedionato)diphenyltin(IV)

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The structure of the octahedral complex bis(2,4-pentanedionato)diphenyltin(IV) $[(C_6H_5)_2Sn(acac)_2]$ was studied in 1965 by McGrady and Tobias[1] and by Nelson and Martin,[2] both groups suggesting a *trans* disposition of the phenyls. The evidence was, however, not conclusive. Nelson and Martin[2] reported the dipole moment of this complex in benzene and in cyclohexane solutions as 3.78 and 4.02 D, respectively. Mainly on the basis of their failure to obtain an optical resolution, they ascribed a *trans* configuration to the complex, and they attributed the apparent orientation polarization to anomalously high atomic polarization effects arising principally from the presence of 2,4-pentanedionato chelate rings.[3] They concluded that either the *trans* isomer is present alone in solution or alternatively the rate of racemization and/or isomerization is very rapid. Recently Moore and Nelson,[4] noting the temperature variation of the measured dipole moment for a number of structurally related Sn complexes, have inferred by analogy that $(C_6H_5)_2Sn(acac)_2$ probably exists as the *cis* isomer. The purpose of this work was to apply the method of dielectric relaxation to ascertain if the observed disparity[2] between the measured total molar polarization and molecular refraction is attributable to a large atomic polarization or to the existence of a permanent electric moment.[5-8] Accordingly dielectric absorption measurements have been made on solutions of $(C_6H_5)_2Sn(acac)_2$ in benzene at frequencies of 3109 and 9400 MHz.

Experimental Section

The complex was prepared from diphenyltin dichloride (Fluka *purum* grade) and sodium 2,4-pentanedionate[9] (mp 226°), as described by McGrady and Tobias[1] except that the reagents

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