of transients (226 560) needed to obtain the signal in Figure 3d compared to the 7477 in Figure 1b. Secondly, the surface area of the α-alumina used in these experiments was 5.5 m^2/g. This surface area has to be considered high for α-alumina. Normal α-alumina has a surface area of less than 3 m^2/g. Hence, one may argue that the surface in the sample used here was contaminated by a transition phase. Using an α-alumina with a surface area of 1 m^2/g did not give rise to a ^{27}Al CP/MAS resonance (Figure 3c). The lack of signal is, in all probability, due to an insufficient number of O_h sites; i.e., a reduction in surface area by a factor of 5 would imply that to obtain the same S/N ratio as depicted in Figure 3d would take 25 times as long or 65.6 days! Therefore, the results depicted in Figure 3d represent a practical lower limit for samples with surface areas in the range from 3 to 5 m^2/g.

In summary, it is clear that there is a great potential to ^{27}Al CP/MAS NMR of alumina surfaces. But the impact of the work goes far beyond the ^{27}Al CP experiment. The success of these experiments supports the notion that surface CP of other nuclides can also be performed with the same relative ease. For example, CP experiments with enriched ^{183}W in HDS catalysts[27] using chemisorbed water as the source of the ^{1}H magnetization, or the CP of enriched ^{95}Mo in the same system using Brønsted sites or chemisorbed water as the source of ^{1}H's, may be envisioned. There are many potential applications, all of which will provide a unique perspective on some complicated and yet very important chemistry.

Acknowledgment. The authors express their appreciation to the NSF for partial support of the work via Awards CHE85-44272 and CHE86-11306. PDE acknowledge many stimulating conversations with Professors Bruce C. Gates (University of Delaware), F. Albert Cotton (Texas A&M University), and Dr. Madan Bhasin (Union Carbide Corp., South Charleston, WV) about various aspects of this work. The sample and spectrum of α-alumina (SA = 5.5 m^2/g) are the courtesy of Ms. Beth A. Huggins (University of South Carolina). Finally, we thank Professor Eric Oldfield (University of Illinois) for sending us a preprint of his ^{17}O cross polarization work. H. D. M. thanks Doty Scientific for support via a graduate student cooperative fellowship.

Registry No. α-Alumina, 1344-28-1; pyridine, 110-86-1.

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Spin Density Characterizations via Analysis of Variable-Temperature ^{183}W NMR for Paramagnetic (^{4}A and ^{5}E) Heteropoly Complexes. Elucidation of Bonding and Quantitation of Ligand-Centered Dipolar Shifts

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Abstract: Temperature dependences (276–350 K) of ^{183}W NMR isotropic shifts have been measured in solution for paramagnetic heteropoly Keggin structures α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ and α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$. The ^{4}A tetrahedral d^7 central Co(II) has three unpaired electrons and the ^{5}E tetrahedral d^6 central Co(III) has four. At room temperature (297 K) the total shift for the Co(II) complex is −887.6 ppm ($\Delta\nu_{1/2}$ = 74 Hz), and it is −1993.7 ppm ($\Delta\nu_{1/2}$ = 26 Hz) for the Co(III) isomorph. This is the first such variable-temperature study of an E system. The results provide strong substantiation for the theoretical approach advanced by Kurland and McGarvey for NMR of nuclei other than ^{1}H or ^{1}D in paramagnetic species. Although in each case the plot of isotropic shifts vs T^{-1} is an excellent straight line, the isotropic shifts are almost entirely *dipolar*, owing to significant unpaired electron spin delocalization from Co to non-s (probably mainly $6p_z$) orbitals of the tungstens. Each of the 12 W's acquires a few hundredths (~0.01–0.06 probably) of an electron's unpaired spin in each complex. This "ligand-centered" (i.e., centered on the observed atoms) dipolar contribution accounts for −780 to −790 ppm of the isotropic shift for the Co(II) complex and −690 to −580 ppm for the Co(III) complex. The Fermi-contact shifts are only −9.9 ± 12.6 and −24 ± 30 ppm, respectively, while the "metal-centered" (Co) dipolar shift is ca. +13 ppm in the Co(II) case and ca. −1300 ppm in the Co(III) species. The smallness of the "metal-centered" dipolar contribution in the Co(II) complex is caused by the absence of g-tensor anisotropy for the very regular $Co^{II}O_4$ central tetrahedron. In contrast, the $Co^{III}O_4$ central tetrahedron is significantly Jahn–Teller distorted, and g-tensor anisotropy leads to a large "metal-centered" term. Values of the diamagnetic contributions to the total shifts were evaluated from the wavelengths of the lowest energy optical absorptions and the straight-line relationship between such wavelengths and chemical shifts that we have evaluated for diamagnetic Keggin tungstates. The overall results are strongly cautionary, for NMR of nuclei other than ^{1}H or ^{1}D, against the commonplace assumption of a preponderance of Fermi-contact contribution on the basis of apparent straight-line plots of isotropic shifts vs T^{-1}. From the standpoint of the chemistry of heteropoly complexes, the results support (1) a presumed similarity between the MO diagrams for $VO(H_2O)_5^{2+}$ and WO_6 units in polyanions and (2) our previous evidence for extensive delocalization of the heteroatom's unpaired electron spins throughout the structures.

This paper reports the first investigation of temperature dependences (276–350 K) of ^{183}W NMR isotropic shifts for paramagnetic species.[1-3] The complexes studied were two Keggin-structure (Figure 1) heteropolyanions: α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ (^{4}A tetrahedral d^7 Co(II) having three unpaired electrons) and α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ (^{5}E tetrahedral d^6 Co(III) having four unpaired electrons). This is also the first such study of an E system.

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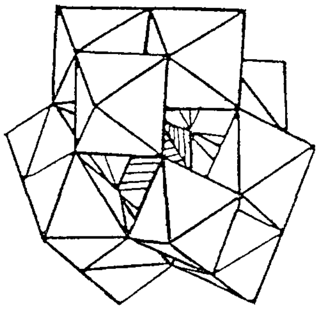

Figure 1. Keggin structure for α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ and α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$. Every vertex of a polyhedron locates the center of an oxygen atom. The Co atom is at the center of the interior hatched tetrahedron. Within each octahedron is a W atom, displaced significantly off-center toward the unshared oxygen atom of its octahedron. In the Co(III) complex the distance between each W and the unshared O attached to it is ~0.7 Å shorter than the distance between the W and the O atom which the W shares with the Co. That difference is ~0.5 Å in the Co(II) complex.

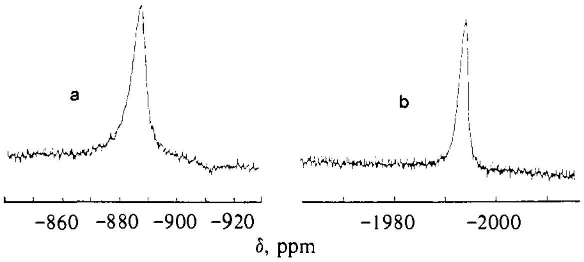

Figure 2. Room-temperature ^{183}W NMR spectra: (a) 0.3 M solution of α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$; (b) 0.3 M solution of α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$.

The excellent potentialities of NMR spectroscopy for tracing unpaired electron density distribution over the ligand atoms of paramagnetic species have been clearly recognized.[4-7] This recognition results in part from the high sensitivity of NMR resonances both to unpaired electron density delocalization (residency) on the observed atoms and to the mechanisms for delocalization. Any quantitative analysis of the isotropic shift in terms of unpaired spin density distribution requires the previous separation of that shift into its contributing terms, namely, the Fermi-contact and dipolar. Several theories have been developed that allow evaluation of each contribution to the isotropic shifts for various cases, in terms of ground-state configurations and relaxation mechanisms, with varying success and acceptance and even with a certain degree of controversy.[4-14] It is in this context that study of temperature dependences of isotropic shifts have been suggested as critical tests for the different theoretical treatments.[13]

Heteropolyanions, which resemble discrete soluble fragments of metal oxide structures of definite size and shape,[15] constitute a large fundamental class of model complexes with which to validate and further advance available theories concerning paramagnetic species. Conversely, elucidation of the isotropic shifts can significantly extend understanding of the role of covalency and of heteroatom electron delocalization fundamental to the bonding, properties, and structures of heteropoly complexes. The ability of heteropoly complexes to stabilize unusual coordination geometries and oxidation states of transition-metal heteroatoms is also pertinent. For example, α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$, used in the present work, presents the very rare case of a d^6 ion in a tetrahedral site, thus exhibiting a ^5E ground state.[15-17] Heretofore no data have been available for temperature dependence of isotropic shifts caused by an E paramagnetic center, for which no explicit theories have been proposed. It will be shown that careful examination of the temperature dependence of isotropic shifts allows evaluation of the various contributions to observed shifts: diamagnetic, Fermi-contact, "metal-centered" dipolar, and "ligand-centered" dipolar.

Our earlier papers[1,18-21] demonstrated the great power of ^{183}W NMR as a tool for polytungstate chemistry. This has led to numerous important papers by others.[22] More recently we have applied multinuclear NMR to elucidating the role and residencies of the delocalized added electrons in heteropoly blue complexes.[23]

The main thrusts of the results reported herein are as follows: (1) The Fermi-contact contribution to the isotropic shift is extremely small in each of the complexes measured, indicating negligible delocalization of unpaired spin density onto tungsten 6s orbitals, in agreement with the currently accepted molecular orbital diagram for these complexes. (2) The dominance of the "ligand-centered" dipolar contribution is demonstrated for the isotropic shift of the Co(II) complex, which contains a regular central $Co^{II}O_4$ tetrahedron as revealed by accurate magnetochemistry[16] and by its X-ray crystal structure.[24] The "ligand-centered" contribution arises from delocalization of unpaired spin onto non-s orbitals of tungsten. This result constitutes a firm substantiation of the theory of NMR isotropic shifts proposed by Kurland and McGarvey[4,11] for nuclei other than ^1H or ^1D. Attempts to fit the data to approaches that ignore the concepts of Kurland and McGarvey lead to very improbable interpretations. (3) In the case of the Co(III) complex, in contrast, the isotropic shift is dominated by the "metal-centered" dipolar contribution, reflecting the distortion of the central $Co^{III}O_4$ tetrahedron. That distortion is expected from the Jahn–Teller theorem, is consistent with accurate magnetochemistry,[16] and is substantiated by an X-ray crystal structure determination.[15,25] (4) For the Co(III) complex both Fermi-contact and dipolar contributions are simultaneously T^{-1} and T^{-2} dependent owing to significant **g**-tensor anisotropy. (5) Taken as a whole, the results show that nearly perfect linearities of δ vs $1/T$ plots over generally accessible temperature ranges do not necessarily indicate Fermi-contact-

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Table I. ^{183}W NMR Shifts for α-$[Co^{x+}O_4W_{12}O_{36}]^{-(8-x)}$, Where $x^+ =$ 2+ and 3+

concn, M			^{183}W NMR shift, ppm	
Co^{2+}	Co^{3+}	temp,[a] K	Co^{2+}	Co^{3+}
0.3		RT[b]	−886[c]	
	0.3	RT[b]		−1994[d]
0.15	0.17	RT[b]	−892	−1994
0.13	0.14	RT[b]	−890	−1994
0.13	0.14	RT[b]	−888	−1992
0.10	0.11	RT[b]	−888	−1994
0.10	0.11	276	−1008	−2207
0.10	0.11	278	−996	−2186
0.10	0.11	280	−985	−2164
0.10	0.11	282	−973	−2141
0.10	0.11	283	−964	−2130
0.10	0.11	285	−957	−2115
0.10	0.11	286	−957	−2111
0.10	0.11	288	−944	−2092
0.10	0.11	290	−924	−2055
0.10	0.11	297	−888	−1994
0.10	0.11	306	−844	−1919
0.10	0.11	316	−802	−1851
0.10	0.11	316	−796	−1840
0.10	0.11	326	−763	−1784
0.10	0.11	326	−757	−1775
0.10	0.11	330	−746	−1759
0.10	0.11	336	−716	−1708
0.10	0.11	340	−707	−1692
0.10	0.11	346	−681	−1649
0.10	0.11	350	−669	−1629

[a] Precision better than 0.5 °C. [b] RT = room temperature. These experiments were run with the temperature control unit off. Temperature at the probehead ca. 24 °C. [c] Line width at half-height, $\Delta\nu_{1/2} = 74 \pm 2$ Hz. [d] Line width at half-height, $\Delta\nu_{1/2} = 26 \pm 2$ Hz.

dominated isotropic shifts, even in those cases with near-zero intercepts. In spite of the apparent excellent straight-line correlations shown by the experimental data presented herein, these isotropic shifts are overwhelmingly dominated by dipolar contributions.

Experimental Section

Spectroscopy. The NMR spectra reported herein were obtained on a Bruker AM 300WB NMR spectrometer operating at a magnetic field of 7.046 T (300 MHz for protons) with 10-mm-diameter sample tubes. The spectrometer was equipped with a calibrated temperature-control unit. Internal deuterium lock signal was provided by the D_2O solvent. Chemical shifts, which are taken as negative toward higher fields, are reported in ppm with respect to an external saturated solution of $Na_2WO_4\cdot 2H_2O$ (ca. 2 M) in 99.7 at. % D_2O at 28 °C and pD 9.1.[19] The acquisition time was 0.475 s, without any added delay between pulses. Typical spectra were 17 241 Hz wide (resolution ±2.1 Hz or 0.16 ppm), and involved accumulation of 3000–5000 transients (requiring 20–40 min). Temperatures between 276 and 350 K were established by using the gas-flow technique.

A duplicate set of spectra, covering the same temperature range, was obtained by using a Bruker WH/HFX-90 NMR spectrometer operating at a magnetic field of 2.114 T (90.02 MHz for protons) and using separately prepared samples. The results were identical with those obtained with the AM 300WB spectrometer.

Preparation of Samples. Very pure analyzed recrystallized samples of α-$K_5[Co^{3+}O_4W_{12}O_{36}]\cdot 11H_2O$ and α-$K_5H[Co^{2+}O_4W_{12}O_{36}]\cdot 15H_2O$ were kindly provided by Dr. Violet E. Simmons Baker. Their syntheses and characterization have been reported previously.[16,17,26] Solutions (0.3 M) of the more soluble sodium salts of these complexes were prepared in previously acidified (H_2SO_4) D_2O by metathesis reactions between slurries of the potassium salts and added solid $NaClO_4$. The $KClO_4$ precipitate was removed by centrifugation.

Results

The experimental results are summarized in Table I. In each α-12-tungstocobaltate complex all the W's are structurally identical, so each spectrum consisted of a single resonance. Figure 2 shows the room-temperature (at the probe head ca. 24 °C) ^{183}W NMR spectra of separate 0.3 M solutions of α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ and α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$. The spectra presented are after exponential multiplication using a line-broadening constant of 2.0 Hz for improved signal-to-noise ratio. Line widths at half-height are $\Delta\nu_{1/2} = 74 \pm 2$ Hz for the Co(II) complex and 26 ± 2 Hz for the Co(III) complex. Figure 3 shows the ^{183}W NMR spectrum of an acidified D_2O solution which was made simultaneously 0.1 M with respect to each complex. Such a mixture was used to obtain all of the isotropic shifts reported.

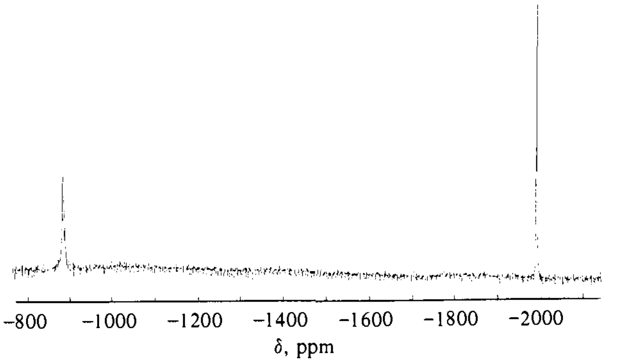

Figure 3. Room-temperature ^{183}W NMR spectrum of a solution simultaneously 0.1 M with respect to α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ and with respect to α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$.

Discussion

Preliminary Considerations. The ^{183}W NMR spectra of α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ and α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ show large upfield shifts,[1,2] ca. 800 and 1900 ppm, respectively, from the resonances of their diamagnetic isomorphs.[18,19] As expected, the line widths in the cases of these paramagnetic complexes are significantly broader (see previous paragraph) than for their diamagnetic isomorphs (for which $\Delta\nu_{1/2} < 1$ Hz). The data in Table I demonstrate that the isotropic shifts for both of these Co complexes are essentially independent of concentration. Further, the spectra show that there is no paramagnetic interaction between the Co^{2+} and Co^{3+} centers in solution. This is consistent with the demonstration by Rasmussen and Brubaker[27] that electron exchange between these heteropoly 12-tungstocobaltates is very slow. The paramagnetic centers are deeply buried inside their respective Keggin structures, and the activation energy for change of CoO_4 dimensions is high.

Theoretical Background. As indicated in the introduction, the first step toward (1) elucidating the distribution of unpaired spin density delocalized from the paramagnetic atom onto the "ligand" atoms (i.e., onto the atoms for which the nuclear magnetic resonances are being observed—W's in the present cases) and (2) elucidating the mechanism for that delocalization is to evaluate separately the individual terms contributing to the chemical shift.[4,5] Isotropic shifts in NMR spectra of paramagnetic species stem from electron–nuclear interaction via direct Fermi-contact hyperfine (scalar) coupling and/or a through-space dipolar (pseudocontact) mechanism. Thus the observed shift can be broken down into three general terms, according to eq 1, where δ_{dia} is the "diamagnetic

$$\delta_{obs} = \delta_{dia} + \delta_{iso} = \delta_{dia} + \delta_{con} + \delta_{dip} \qquad (1)$$

reference shift", usually estimated as the chemical shift for an isostructural diamagnetic species. δ_{con} and δ_{dip} are the contact and dipolar terms, which make up the isotropic shift, δ_{iso}. Small uncertainties in δ_{dia} are usually insignificant relative to the large size of δ_{iso}.

Fermi-contact shifts are a direct measure of the unpaired spin density delocalized *onto s orbitals* around the resonating nucleus and are taken as evidence of "metal-ligand" covalency.

Any dipolar contribution arises from through-space interaction between an electronic magnetic moment and the observed nucleus.

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Dipolar contributions can vanish in magnetically isotropic systems as a result of molecular tumbling in solution. It has been stated that dipolar shifts should exhibit the same temperature dependence as do the susceptibility anisotropies.[28] The isotropic shifts of paramagnetic complexes with no zeroth-order spin–orbit coupling effects (i.e., non-T states) and spin quantum number, S, equal to or greater than 1 can be analyzed in a simple way from their temperature dependences. In those cases where the foregoing two conditions are met (no T states with $S \geq 1$), the ground term will be split into levels the separation of which is much smaller than kT (i.e., undergo zero-field splitting, ZFS). Then it can be shown[4] that the mixing of these levels by the magnetic field allows the temperature dependence of the isotropic shift to be broken down into a Curie-law-type term (varying as T^{-1}) and a term depending on T^{-2}, as shown in eq 2. This, for example, has been shown to

$$\delta_{\text{iso}} = aT^{-1} + bT^{-2} \qquad (2)$$

fit ^{1}H NMR spectra of lanthanide complexes, for which the dipolar term often makes by far the predominant contribution to the shift, the contact term being negligible.[28]

Even in the absence of significant magnetic anisotropy, ZFS lifts the degeneracy of the ground state and often leads to dipolar shifts that exhibit characteristic T^{-2} dependence.[12] Tetrahedral Co(II), with ^{4}A ground state, small ^{4}A–^{4}T separation, and large spin–orbit coupling constant, frequently shows significant dipolar shifts arising from mixing of ground and excited states.[10,29]

Equation 2 indicates that any curvature in the Curie plot (isotropic shift vs T^{-1}) can be taken as evidence for a dipolar contribution. Unfortunately, experimental data frequently do not show such curvatures, even in cases where dipolar terms are expected to be important, because experimental data are usually available only over a relatively small range around room temperature. Since there is no reason to expect a temperature-independent contribution to δ_{iso}, eq 2 indicates that extrapolation of a plot of T^{-1} vs δ_{iso} should go through the origin. Therefore, if extrapolation of such an apparently linear plot of experimental points has a nonzero intercept, a dipolar contribution is indicated.

Although the foregoing applies generally to NMR spectra of paramagnetic systems, Kurland and McGarvey[4,11] have elucidated important additional factors for NMR-active nuclei *other than protons*. For protons, only 1s orbitals can be involved in spin-transfer mechanisms, but for other atoms unpaired spin density is also expected to reside in p, d, and/or f orbitals of the "ligand" (i.e., the observed) atoms. Unpaired spin density in non-s orbitals does not significantly contribute to the Fermi-contact term (except for some small radial correlation effects[30]), but a substantial contribution to the dipolar term is certainly expected. Kurland and McGarvey[4,11] pointed out that although the unpaired spin density at the "ligand" atom may be much less than that at the paramagnetic metal atom, $\langle r^{-3} \rangle$ (r = the atomic orbital radius) is certainly much larger than $\langle R^{-3} \rangle$ (R = distance between "ligand" atom and paramagnetic atom). Therefore, the dipolar contribution originating from unpaired spin density in non-s orbitals centered on the observed nucleus (i.e., the "ligand-centered" dipolar contribution) may be not only important but, in cases of isotropic systems, even be greater than the "metal-centered" dipolar contribution. Consequently, when NMR of nuclei other than protons are observed in paramagnetic species, eq 1 must be expanded by subdividing δ_{dip} into a "ligand-centered" dipolar contribution, $\delta_{\text{dip}}{}^{\text{L}}$, and a "metal-centered" dipolar contribution, $\delta_{\text{dip}}{}^{\text{M}}$, yielding

$$\delta_{\text{obs}} = \delta_{\text{dia}} + \delta_{\text{con}} + \delta_{\text{dip}}{}^{\text{M}} + \delta_{\text{dip}}{}^{\text{L}} \qquad (3)$$

Diamagnetic Contributions. The diamagnetic reference shifts for these heteropoly complexes can be readily evaluated by interpolation by using the straight-line plot of lowest energy UV absorption wavelengths in water solutions vs ^{183}W δ's for a series of diamagnetic Keggin complexes,[19] as predicted by the Jameson–Gutowsky equation.[31] This procedure yields $\delta_{\text{dia}} = -109$ ppm for α-$[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{6-}$ and $\delta_{\text{dia}} = -81$ ppm for α-$[\text{Co}^{3+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{5-}$.

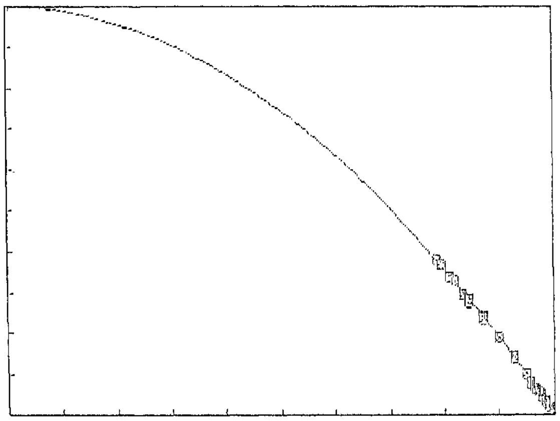

Figure 4. Plot of ^{183}W NMR isotropic shifts vs T^{-1} for α-$[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{6-}$. The line represents the best fit to eq 2.

α-$[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{6-}$ Isotropic Shifts. Figure 4 is a plot of isotropic shifts, δ_{iso} (eq 1) vs $1/T$ for the Co(II) complex. Although the experimental points show an excellent straight-line correlation, that is an artifact of the limited temperature range possible. That the plot over the entire temperature range is in fact decidedly nonlinear is shown by the large nonzero intercept (+590 ppm) of the extrapolated straight line. This large intercept indicates a significant dipolar contribution. The line in Figure 4 is the best least-squares fit of the experimental data to eq 2 (which requires a zero intercept and constant values of a and b). The curve-fitting analysis yielded $a = -2.96 \times 10^{-3} \pm 3.76 \times 10^{-3}$ and $b = -67.95 \pm 0.97$, with a correlation coefficient of 0.99986.

The complete expressions for ^{1}H contact and for ^{1}H dipolar shifts for the ^{4}A ground state (tetrahedral Co(II)), in a complex with axial symmetry, are[4,13]

$$\delta_{\text{con}} = -\frac{5\bar{g}\beta A}{4\hbar\omega kT}\left[1 - \frac{4(g_{\parallel} - g_{\perp})D}{15\bar{g}kT}\right] \qquad (4)$$

$$\delta_{\text{dip}} = \frac{5\beta^2(g_{\parallel}{}^2 - g_{\perp}{}^2)}{12kT}\,\frac{(1 - 3\cos^2\theta)}{R^3}\left[1 - \frac{4(g_{\parallel}{}^2 + \frac{1}{2}g_{\perp}{}^2)D}{5(g_{\parallel}{}^2 - g_{\perp}{}^2)kT}\right] \qquad (5)$$

where A is the hyperfine coupling constant (A/h has units of hertz), D is the zero-field splitting, R is the distance between the paramagnetic atom and the nucleus being observed, θ is the angle between the principal symmetry axis of the Keggin structure and the vector from the Co to the "ligand" W atom, and ω is the magnetogyric ratio of the nucleus under observation. The other terms have their usual meanings. Since eq 4 and 5 are for *proton* isotropic shifts, the "ligand-centered" term, discussed above, is not yet included.

The tetrahedral CoO_4 paramagnetic center in α-$[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{6-}$ is highly regular[16,24] and consequently $g_{\parallel} \cong g_{\perp}$, so that eq 4 and 5 simplify, for this case, to

$$\delta_{\text{con}} = -\frac{5\bar{g}\beta A}{4\hbar\omega kT} \qquad (6)$$

$$\delta_{\text{dip}} \cong \left[\frac{3\cos^2\theta - 1}{3R^3}\right]\frac{\beta^2(g_{\parallel}{}^2 + \frac{1}{2}g_{\perp}{}^2)D}{(kT)^2} \qquad (7)$$

In this complex $\theta \cong 30°$, $R \cong 3.6 \times 10^{-8}$ cm, ω (the magnetogyric

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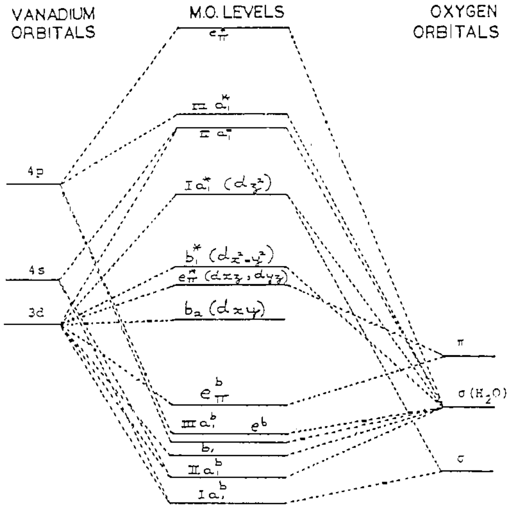

Figure 5. MO diagram for $VO(H_2O)_5^{2+}$ (from ref 34).

ratio for W) = 1.11×10^3 rad G^{-1} s^{-1}, and[32] $g_\parallel \cong g_\perp \cong 2.2$.

After substitution, eq 6 and 7 combine to yield

$$\delta_{iso} = -1.04 \times 10^{-6}(A/hT) + 2.93 \times 10^{14}(D/T^2) \qquad (8)$$

Using the values of a and b evaluated above by curve fitting of the experimental data to eq 2, it is possible to calculate from eq 8 that $A/h = (2.84 \pm 3.6) \times 10^3$ Hz and D = -1167 ± 17 cm^{-1}. This preposterously large value for D (the ZFS) demonstrates that the "ligand-centered" dipolar contribution cannot be ignored, as will be discussed below. Note that the standard deviation for the value of A/h is greater than the term's small magnitude, indicating that the contribution of any Fermi-contact term is essentially zero, although the situation also prevents a confident assignment of sign to the hyperfine coupling constant.

It is well-known that the magnitude of the hyperfine coupling constant provides a direct measure of unpaired spin delocalized onto s orbitals centered at the resonating nucleus.[5] Morton and Preston[33] have calculated the isotropic hyperfine interaction for the more important nuclei of elements from He to Bi. For a unit spin density in the tungsten 6s valence orbital the isotropic coupling constant is 5780 MHz. Thus the isotropic hyperfine coupling reported in the previous paragraph represents a valence 6s unpaired spin density of only 1.1×10^{-6} to 1.3×10^{-7} electron per W atom, or essentially zero.

This is eminently consistent with the MO diagram (Figure 5) calculated by Ballhausen and Gray[34,35] for $VO(H_2O)_5^{2+}$, which has been widely accepted as the description of bonding in the WO_6 octahedra of heteropoly tungstates. Recently, molecular orbital diagrams have been calculated for various polymolybdates, including the Keggin structure.[36] The diagrams for the $Mo^{6+}O_6$ units were essentially identical with that for the Ballhausen and Gray vanadium complex, especially with respect to the details of importance to the present work.

In the Keggin structure 12-tungstocobaltates each W atom is very significantly displaced[15,24,25] in its WO_6 octahedron toward the exterior terminal oxygen of that WO_6 and that oxygen is double bonded to the W. The distance from each W to the interior oxygen (which is also one of the oxygens of the CoO_4) is correspondingly elongated. This leaves the four equatorial oxygens of the WO_6 at approximately equal intermediate distances from the W.[15,24,25] This arrangement serves to identify the various oxygens attached to each W in the MO diagram.

Examination of Figure 5 indicates that the bond between each W and the oxygen of the CoO_4 tetrahedron involves only the $6p_z$ tungsten orbital so that the bond has essentially zero tungsten s orbital participation. The absence of a significant Fermi-contact contribution to the isotropic shift lends strong experimental support to the MO bonding description.

The fact that treatment in terms of eq 7 yields a very unrealistically large D (ZFS) value (which would be expected to be about 2–3 orders of magnitude smaller) constitutes, actually, a strong corroboration of the proposals of Kurland and McGarvey concerning non-hydrogen nuclei. The large calculated D shows that it is not valid in the present case to ascribe the whole dipolar shift to ZFS and that important contributions to the dipolar term have been neglected. In fact eq 7 and 8 apply only to cases wherein only s orbitals of the observed atoms have acquired the delocalized unpaired electron density. The foregoing treatment for the ^{183}W NMR is incomplete because it ignores contributions from unpaired electron density in p and/or d orbitals around the W nucleus and it ignores the unpaired electron density on the oxygens of the distorted WO_6 group.

The WO_6 molecular orbitals participating in the unpaired electron transfer between Co and W contain only p and d orbitals of tungsten (primarily the p_z of W according to Figure 5). This "ligand-centered" dipolar contribution is proportional to the susceptibility anisotropy, and it can be described as a second-order Zeeman term. Such splitting allows mixing of "ligand" ground and excited states, and thus it is also proportional to T^{-2}, according to the following equation:[37]

$$\delta_{dip}{}^{L} = -\frac{\beta P \alpha \rho (g_\parallel{}^2 + \frac{1}{2}g_\perp{}^2)_W D}{6\omega(kT)^2} \qquad (9)$$

where P, the anisotropic hyperfine interaction for the "ligand" atom, is proportional to the average value of r^{-3} for its non-s orbitals. P has been calculated by Morton and Preston[33] as $P = 1.03 \times 10^9$ rad s^{-1} for ^{183}W. α is the angular factor for the real atomic orbitals implicated in the unpaired spin-transfer process[33] and $\alpha(p_z) = {}^4/_5$. The ESR spectrum of the one-electron reduced heteropoly blue species α-$[Co^{2+}O_4W_{12}O_{36}]^{7-}$ at 77 K gives $g_W = 1.79$ in addition to Co(II) signals.[38] The fraction of an unpaired electron's spin delocalized to the non-s orbital is represented by ρ. The importance of the relative sites of R and r has been explained above.

There is a third, more minor, contribution to the dipolar term to be considered in the present case, namely, that coming from unpaired electron spin density delocalized onto the oxygen atoms of the WO_6 octahedra, which are distorted to lower than T_d symmetry.[15,24] In view of its R^{-3} dependence, this oxygen contribution to the overall W dipolar shift is expected to be very small.

Thus, if "ligand-centered" (W) as well as the "metal-centered" (Co) contributions are considered, the total dipolar shift is given by substitution in a combination of eq 7 and 9, which yields

$$\delta_{dip} = (2.93 \times 10^{14} - 2.90 \times 10^{17}\rho)(D/T^2) \qquad (10)$$

Use can now be made of the value of $b = -67.95 \pm 0.97$ obtained above by curve-fitting. This yields an equation with two unknowns (D is in ergs):

$$-67.95 = (2.93 \times 10^{14} - 2.90 \times 10^{17}\rho)D \qquad (11)$$

An exact determination of the actual unpaired spin delocalized onto each tungsten atom (ρ) would be possible if an independent determination of the ZFS were available. However, a good estimate can be arrived at. Table II gives values of ZFS (i.e., D) calculated from eq 11 for various fractions of an unpaired spin delocalized onto each W, i.e., ρ's, covering from 0.1 to 10^{-5} electron. Table II also gives the corresponding magnitudes of $\delta_{dip}{}^{M}$, $\delta_{dip}{}^{L}$, and the total calculated shift for each ρ at 24 °C.

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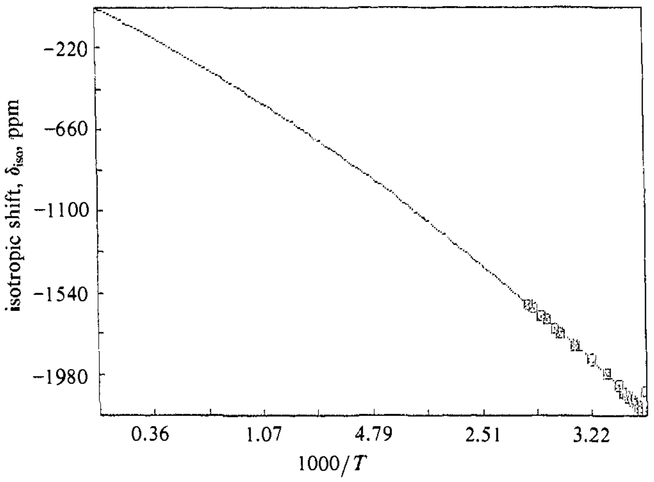

Figure 6. Plot of ^{183}W NMR isotropic shifts vs T^{-1} for α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$. The line represents the best fit to eq 2.

Tetrahedral Co(II) complexes usually exhibit ZFS parameters, D's, sufficiently large to give narrow NMR lines,[16,28] D being within the range of ±30 cm^{-1} for cases with axial symmetry.[39] Thus, the data for α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ and the evaluations in Table II point to an unpaired spin transfer of the order of a few hundredths of an electron onto each tungsten's non-s, primarily 6p$_z$, orbitals.

If, for example, 20 cm^{-1} is taken as a reasonable value for the ZFS parameter, D (or $\rho \cong 0.06$ electron), the observed shift for α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ at 24 °C (−887.6 ppm) can be interpreted as arising from the following contributions:

$$\delta_{dia} = -109 \text{ ppm} \quad \delta_{con} = -9.94 \pm 12.6 \text{ ppm}$$

$$\delta_{dip}{}^{M} = +13 \text{ ppm} \quad \delta_{dip}{}^{L} = -783 \text{ ppm}$$

In summary, it may be seen from Table II that the "ligand-centered" dipolar shift, $\delta_{dip}{}^{L}$, is the overwhelming contribution in any case and that each W receives a few hundredths of an unpaired electron spin.

To our knowledge, this is the first case for which the magnitudes of "ligand-centered" and of "metal-centered" dipolar contributions have been separately evaluated, and the relevance of the "ligand-centered" term established for a complex in which that contribution predominates over all other contributions.

From the standpoint of the chemistry of heteropoly complexes the results accord well with the regularity of the central $Co^{2+}O_4$ tetrahedron (which accounts for the relatively low "metal-centered" dipolar contribution). They also accord well with the observation of an unusually large nephelauxetic effect in these cobalt complexes[16] despite the relative isolation of the CoO_4 central tetrahedron, from which the bonds to the W atoms are unusually long.[15,24] The latter condition also helps to explain the small Fermi-contact term.

α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ Isotropic Shifts. Figure 6 is a plot of isotropic shifts, δ_{iso} (ppm) vs T^{-1} for the D_2O solution of the sodium salt of α-12-tungstocobaltate(III). The paramagnetic center in this complex is high-spin tetrahedral Co(III) having four unpaired electrons and a ^{5}E ground state.[16,17] E states are highly susceptible to Jahn–Teller distortions. Assuming a large enough splitting of the ^{5}E ground state into ^{5}A and ^{5}B states under the tetragonal distortion found in the X-ray structure,[15,25] the calculation of isotropic shifts can be treated as for a nondegenerate ground state.[13] Thus, although a complete expression for the isotropic shift for a ^{5}E state has, to our knowledge, not yet been derived, an approximate expression can be obtained by simply interpolating into the coefficients given[4,13] for nondegenerate states with S = 1, $^3/_2$, and $^5/_2$, to obtain approximate coefficients for S = 2 (nondegenerate state approximation). The following expressions will be used in this discussion:

$$\delta_{con} = -\frac{2\bar{g}\beta A}{\hbar\omega kT}\left[1 - \frac{0.46(g_{\parallel} - g_{\perp})D}{\bar{g}kT}\right] \qquad (12)$$

$$\delta_{dip}{}^{M} = \frac{2\beta^2(g_{\parallel}{}^2 - g_{\perp}{}^2)(1 - 3\cos^2\theta)}{3kTR^3}\left[1 - \frac{1.38(g_{\parallel}{}^2 + \frac{1}{2}g_{\perp}{}^2)D}{(g_{\parallel}{}^2 - g_{\perp}{}^2)kT}\right] \qquad (13)$$

where, as a first approximation, only s unpaired spin density on the observed atom is considered.[40] If the g-tensor anisotropy is also considered negligible, as for the Co(II) analogue, eq 12 and 13 reduce to

$$\delta_{iso} = -\frac{2\bar{g}\beta A}{\hbar\omega kT} + \left[\frac{3\cos^2\theta - 1}{3R^3}\right]\frac{2.76\beta^2(g_{\parallel}{}^2 + \frac{1}{2}g_{\perp}{}^2)D}{(kT)^2} \qquad (14)$$

where the first term corresponds to the Fermi-contact contribution and the second term expresses the "metal-centered" dipolar contribution. Taking $R = 3.6 \times 10^{-8}$ cm, $\theta \cong 30°$, and[32] $g = 2.07$, eq 14 becomes

$$\delta_{iso} = -(1.57 \times 10^{-6})(A/hT) + (7.17 \times 10^{14})(D/T^2) \qquad (15)$$

The curve fitting of the experimental isotropic shifts to eq 2 yields $a = -0.400 \pm 0.028$ and $b = -50.2 \pm 7.2$ (correlation coefficient = 0.9984). Substitution into eq 15 gives

$$0.40 = 1.57 \times 10^{-6}(A/h) \qquad 50.2 = 7.17 \times 10^{14}D$$

This would correspond to a hyperfine coupling constant of 2.55 × 10^5 Hz and a ZFS of −352.4 cm^{-1}. Neither of these values is acceptable, which shows that important contributions to both Fermi-contact and dipolar shift terms have been neglected in this initial consideration.

The hyperfine coupling constant indicated by the foregoing approach is about 2 orders of magnitude greater than that obtained in the previous section for the isomorphous Co(II) complex. Since the Co(II) and Co(III) complexes are isomorphs, the same spin-transfer mechanism is expected to operate in each. Then, Fermi-contact couplings (and s unpaired spin densities) should be proportional to $S(S + 1)$. That is

$$(A/h)_{Co^{3+}} = 1.6(A/h)_{Co^{2+}} \cong (4.54 \pm 5.7) \times 10^3 \text{ Hz} \qquad (16)$$

which result is about 100-fold smaller than the magnitude obtained by fitting experimental data for the Co(III) complex to eq 2 and substituting into eq 15. The magnitude of $(A/h)_{Co^{3+}}$ calculated above from $(A/h)_{Co^{2+}}$ is again very small. The apparently anomalous preliminary calculation can be rationalized as arising from the "filtration" of some part of the dipolar component into the T^{-1} term. In fact, the complete expression for the isotropic shift (see eq 12 and 13) shows that both contact and dipolar shifts are simultaneously T^{-1} and T^{-2} dependent, the T^{-1} term in eq 14 being a valid approximation for the Fermi-contact shift only in those cases where the g-tensor anisotropy is negligible. While the $Co^{II}O_4$ tetrahedron in α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ is very regular,[16,24] the $Co^{III}O_4$ tetrahedron has considerable dynamic as well as static Jahn–Teller distortion.[15,16,25] This distortion is confidently expected

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[40] After submission of this work, one of the referees suggested the following complete expression for the contact and dipolar shifts in S = 2 systems:

$$\delta_{con} = -\frac{2\bar{g}\beta A}{\hbar\omega kT}\left[1 - {}^{7}/_{15}\frac{(g_{\parallel} - g_{\perp})D}{\bar{g}kT}\right]$$

$$\delta_{dip}{}^{M} = \left[\frac{1 - 3\cos^2\theta}{3R^3}\right]\frac{2\beta^2(g_{\parallel}{}^2 - g_{\perp}{}^2)}{kT}\left[1 - {}^{7}/_{5}\frac{(g_{\parallel}{}^2 + \frac{1}{2}g_{\perp}{}^2)D}{(g_{\parallel}{}^2 - g_{\perp}{}^2)kT}\right]$$

These equations give essentially the same results as those obtained by the interpolation process described in the text, i.e., $^7/_{15} \cong 0.46$ and $^7/_5 \cong 1.38$.

Table II. ZFSs (i.e., D) Calculated for Various Values of ρ (Fraction of Unpaired Spin per W) and Corresponding Contributions to the Isotropic Shifts for α-$[Co^{2+}O_4W_{12}O_{36}]^6$

ρ, electron	ZFS (D), cm^{-1}	$\delta_{dip}{}^M$, ppm	$\delta_{dip}{}^L$, ppm	δ_{total},^{a} ppm
1.0×10^{-5}	−1179.1	−778.0	7.7	−889
1.0×10^{-4}	−1295.7	−854.9	84.6	−889
5.0×10^{-4}	−2311.2	−1524.9	754.6	−889
1.0×10^{-3}				
5.0×10^{-3}	295.6	195.1	−965.3	−889
1.0×10^{-2}	131.2	86.6	−856.8	−889
2.0×10^{-2}	62.1	41.0	−811.2	−889
3.0×10^{-2}	40.7	26.8	−797.1	−889
3.5×10^{-2}	34.7	22.9	−793.1	−889
3.8×10^{-2}	31.9	21.0	−791.3	−889
4.0×10^{-2}	30.3	20.0	−790.2	−889
4.5×10^{-2}	26.8	17.7	−787.9	−889
5.0×10^{-2}	24.1	15.9	−786.1	−889
5.5×10^{-2}	21.8	14.4	−784.6	−889
6.0×10^{-2}	20.0	13.2	−783.4	−889
6.5×10^{-2}	18.4	12.2	−782.4	−889
7.0×10^{-2}	17.1	11.3	−781.5	−889
7.5×10^{-2}	15.9	10.5	−780.7	−889
8.0×10^{-2}	14.9	9.8	−779.9	−889
9.0×10^{-2}	13.2	8.7	−778.9	−889

^{a}The total shifts were calculated by using $\delta_{con} = -9.9$ and $\delta_{dia} = -109$ ppm. See text.

to cause significant **g**-tensor anisotropy. Consequently, dipolar as well as contact contributions to the isotropic shift should be both T^{-1} and T^{-2} dependent. Therefore, eq 12 and 13 should be used in this case instead of the simplified eq 14 to give a complete (although still approximate) expression.

The considerations set forth in the previous paragraph also apply to the dipolar term for which the first (i.e., T^{-1}) term is not negligible when **g**-tensor anisotropy is significant.

As in the case of the Co(II) complex, the "ligand-centered" term must also be taken into consideration. As shown above, its neglect in the case of the Co(III) complex also leads to an improbably high ZFS. An approximate expression for the "ligand-centered" (W) contribution for a ^{5}E system is given by

$$\delta_{dip}{}^L = -\frac{1.38\beta P\alpha\rho(g_{\parallel}{}^2 + \frac{1}{2}g_{\perp}{}^2)_W D}{\omega(kT)^2} \tag{17}$$

where all the symbols have the same meanings as in eq 9. One-electron heteropoly blue α-12-tungstates generally give ESR spectra with g_W values of ~1.8, with only small deviations.[41] After appropriate substitutions, eq 17 gives

$$\delta_{dip}{}^L = -2.43 \times 10^{18}\rho(D/T^2) \tag{18}$$

Combination of eq 12, 13, and 18 with the values $a = -0.40$ and $b = -50.2$, obtained from the curve fitting, leads to the following two equations:

$$0.40 = 1.57 \times 10^{-6}(A/h) + 1.11 \times 10^{-2}(g_{\parallel}{}^2 - g_{\perp}{}^2) \tag{19}$$

$$-50.2 = [2.54 \times 10^9(g_{\parallel} - g_{\perp})(A/h) + 1.12 \times 10^{14}(g_{\parallel}{}^2 + \tfrac{1}{2}g_{\perp}{}^2) - 2.43 \times 10^{18}\rho]D \tag{20}$$

Substitution of the value for A/h, previously obtained from eq 16, into eq 19 gives $g_{\parallel}{}^2 - g_{\perp}{}^2 = 35.4$. The extent of **g**-tensor anisotropy can often be obtained directly from ESR spectra. Unfortunately, to our knowledge, all previous attempts to obtain the ESR spectrum of α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ have been unsuccessful even at liquid nitrogen temperature. This is apparently a consequence of intermolecular magnetic interactions in the solid that lead to extensive line broadening. We have therefore undertaken a low-temperature ESR investigation[42] of the potassium α-12-tungstocobaltates doped into the potassium salt of their diamagnetic isomorph, α-$[B^{3+}O_4W_{12}O_{36}]^{5-}$. An initial result is the ESR spectrum of α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ at liquid nitrogen temperature. Analysis of this preliminary spectrum gives (true, molecular) g values of $g_{\parallel} = 5.3$–6.1 and $g_{\perp} \cong 0.83$, corresponding to a **g**-tensor anisotropy, $g_{\parallel}{}^2 - g_{\perp}{}^2$, between 27 and 37, in very good substantiation of the prediction obtained from the foregoing analysis.

The magnitude of ρ in eq 20 can, for the Co(III) complex, reasonably be expected to be of the same order of magnitude as (but probably a little greater than) ρ for the Co(II) isomorph, for which a minimum of 0.04 electron is expected to be delocalized onto each W atom. See Table II. Then, substitution into eq 20 of appropriate values ($g_{\parallel} \cong 6.1$; $g_{\perp} \cong 1.7$; $A/h \cong 4.54 \times 10^3$ Hz; $\rho \cong 0.04$ electron) provides 2.7 cm^{-1} as an upper limit for the ZFS parameter D.

The observed total shift for α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ at 24 °C is −1993.7 ppm, of which −81 ppm is δ_{dia}. The foregoing treatment, via eq 12, 13, and 17, shows that $\delta_{con} = -24 \pm 30$ ppm and, for ρ ranging from 0.01 to 0.1 electron, D ranges from 12.7 to 1.06 cm^{-1}, while $\delta_{dip}{}^M$ falls in the range −1200 to −1300 ppm, and $\delta_{dip}{}^L$ lies between −694 and −584 ppm.

Thus, as in the case of the Co(II) complex, while solutions for the various contributions to the isotropic shift are not exact, their relative sizes and approximate values are clearly revealed.

These results show, as for the α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ complex, that the Fermi-contact contribution is very small (at most 2% or essentially zero), contrary to any first impression given by the apparent "linearity" of the plot of experimental isotropic shifts vs T^{-1}.

Anisotropy of the **g**-tensor resulting from intramolecular reorientation and a combination of static and dynamic Jahn–Teller distortions of the $Co^{III}O_4$ central tetrahedron, which is not present in the $Co^{II}O_4$ tetrahedron, is responsible for the inversion of the relative magnitudes of "ligand-centered" and "metal-centered" dipolar shifts in the two isomorphous α-12-tungstocobaltates. In the Co(II) complex the isotropic shift is dominated by the "ligand-centered" contribution, while the predominant term for the ^{5}E Co(III) complex is the "metal-centered" dipolar shift. The total estimate of the "ligand-centered" dipolar contribution, which indicates the extent of delocalization of unpaired electron spin through the complex, is considerable and is of the same order of magnitude for each complex.

The line widths observed for α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ (74 Hz) and α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ (26 Hz) provide an independent qualitative substantiation of the foregoing results and interpretations. Since the paramagnetic line width is proportional to R^{-6}, the only significant contribution that is expected to affect the nuclear relaxation mechanisms is the "ligand-centered" dipolar shift. The square root of the ratio of the line widths should, then, give the ratio of the δ_{dip} terms for the two complexes, except for a correlation factor that affects only the relaxation but not the shift.[43] This correlation factor is expected to be smaller for the ^{5}E Co(III) case, owing to modulation by the Jahn–Teller effect. In fact, the square root of the ratio of line widths (1.7) for the Co(II) complex/Co(III) complex, correlates very well with the ratio of "ligand-centered" dipolar shifts found for the same complexes (1.1–1.3) if the latter value is multiplied by a correlation factor a little greater than unity, as expected.

Doddrell et al.[44] have demonstrated by a qualitative interpretation of experimental evidence the necessity of considering "ligand-centered" effects on ^{13}C relaxation mechanisms in paramagnetic complexes.

These results constitute, in numerous ways, strong validation of the theory of Kurland and McGarvey regarding isotropic shifts of nuclei other than protons or deuterons.

Acknowledgment. We thank Dr. Robert J. Kurland for carefully

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Observation of Anion Spinning in the Dynamic ^{31}P NMR Spectra of Fluorine-Bridged SbF_6^-, BF_4^-, and PF_6^- Adducts of $R_3P(CO)_3(NO)W^+$. Implications for Barriers to Ionization and the Formation of Ion Pairs and Free Ions in Methylene Chloride and Hexane Solution

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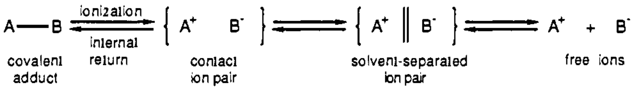
Abstract: An NMR method to measure ionization and ion-pair separation barriers is described. Variable-temperature ^{31}P NMR spectra on *mer*-(*cis*-R_3**P**)$(CO)_3(NO)W(\mu\text{-F})EF_n$ (EF_n = SbF_5, R = Me (**1a**), *n*-octyl (**1b**); R = Me, EF_n = BF_3 (**2**), PF_5 (**3**)) reveal two EF_{n+1}^- exchange processes in methylene chloride and hexane; rate constants are determined from line-shape analyses and the corresponding activation parameters are derived. The low-temperature intramolecular exchange process gives a doublet for the R_3P phosphorus atom due to coupling to the μ-F ligand in the slow-exchange limit, and a septet for **1a**, **1b**, and **3**, and a quintet for **2**, in the fast-exchange limit due to anion "spinning"; the same process gives a doublet of sextets for the PF_6^- phosphorus atom of **3** in the slow-exchange limit and a septet in the fast-exchange limit. The high-temperature intermolecular exchange process results in collapse of each R_3P multiplet to a singlet. For the low-temperature process ΔG^* follows the expected order SbF_6^- (10.4 kcal/mol for **1a**) > BF_4^- (9.8 kcal/mol) > PF_6^- (9.1 kcal/mol). Two isokinetic reaction series are found for intramolecular exchange, one for Me_3P adducts **1a**, **2**, and **3** in methylene chloride, and one for the SbF_6^- adducts **1a** and **1b** in both methylene chloride and hexane. In the former case decreased anion coordinating ability causes the transition state to move toward lower enthalpy and entropy, while in the latter case the same result is effected by increased steric bulk and lower solvent polarity. For each reaction the intramolecular ΔH^* is higher than that for the corresponding intermolecular process; essentially similar activation parameters are observed for each high-temperature reaction, with $\Delta H^* \approx 5.6$ kcal/mol and $\Delta S^* \approx -35$ eu. These data are consistent with W–F bond cleavage in the low-temperature process to give ion pairs, followed by ion-pair separation to give free ions in the high-temperature process. This ionization scheme is consistent with theoretical calculations of dissociation constants for formation of free ions from ion pairs in methylene chloride, but not in hexane. A different mechanism is proposed for this latter case, namely, bimolecular anion exchange in reversed micelles of **1b**. A complete free energy and enthalpy diagram is constructed for the methylene chloride ionizations.

Investigation of ionization and ion-pairing phenomena continues to be an area of active research, despite work going back over half a century.[1-12] As illustrated in Scheme I, current interest centers on rates of ionization of the covalent adduct to give contact and/or solvent-separated ion pairs, and rates of separation of the ion pairs via diffusion of the individual ions out of the solvent cage to give the free ions. The existence of such measurable rates implies that the ion pair exists as a true intermediate having a barrier to

Scheme I



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