^{183}W NMR of Heteropoly- and Isopolytungstates. Explanations of Chemical Shifts and Band Assignments. Theoretical Considerations[1]

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Abstract: Extremely sharp, δ-sensitive spectra, taken on a Bruker WH/HFX 90 FT instrument, demonstrate the importance of ^{183}W NMR for the intricate, expanding polytungstate field. Chemical shift differences are dominated (1) by availability of paramagnetic contributions from low-lying excited states for mixing with ground states and (2) by degree of electronic anisotropy at the sites of respective W's. Inductive charge variation on the W atoms or their neighbors is not a significant factor. In the single-resonance isomorphous α-12-heteropolytungstates ("Keggin" structures), the anisotropy factor is constant, so over a sizable series of compounds an excellent linear relationship is obtained between ^{183}W δ's and the wavelength of the lowest energy optical absorption for each complex. This unambiguously substantiates existing theoretical predictions relative to chemical shifts of transition metals. Both the diamagnetic and paramagnetic components of the shielding constant may be evaluated from the graph. Removal or substitution of one W atom to form 11-tungsto or 17-tungstodihetero species decreases the availability of excited states, producing a general influence toward upfield shift for all the W's; but superimposed on this is a downfield shift of similar magnitude for those W's near the vacancy or substituted atom, caused by increased electronic anisotropy at those sites. Substitution of certain atoms having quadrupolar nuclei, e.g., V^{5+}, for W atoms provides a mechanism for rapid relaxation of the adjacent W atoms, broadening their signals, sometimes into nonobservability. This provides a powerful structural probe. It is demonstrated that the very sharp spectra enable structural conclusions from variations in small two-bond coupling constants. The line broadenings, relative coupling constants, and relative δ's permit many unambiguous line assignments. The latter show that previous assignments and their rationalizations are incorrect.

That ^{183}W NMR holds high potential for development as a new tool for polytungstate chemistry was shown by our first communication[2] on this subject. The technique will elucidate molecular and electronic structures as well as reactions of heteropoly- and isopolytungstates in solution. The big variety and structural intricacies of that large category of complexes, not to mention other tungsten compounds, provide wide and interesting scope for use of the very sharp ($\Delta\nu_{1/2} \simeq 0.2$–0.4 Hz) and δ-sensitive[2] ^{183}W spectra. Although ^{183}W has very low NMR sensitivity (nuclear receptivity only 1.04×10^{-5} that of ^{1}H), favorable factors include simplicity of spectra derived from the nuclear spin being $^{1}/_{2}$, the isotope's reasonable natural abundance (14.27%), and the fact that it is the only NMR-active isotope in natural W. Further, the existence of heteropolytungstates that incorporate, often in isomorphous series of soluble complexes, nearly all the nonmetals and transition elements, including such NMR-active nuclei as ^{31}P, ^{51}V, ^{17}O, ^{11}B, etc., offers valuable potential for extension of NMR theory.

Our second communication[3] showed examples of the power of ^{183}W NMR spectra to settle definitely some difficult controversies in the heteropolytungstate field. It also showed the clear determination of very small two-bond coupling constants and foreshadowed their use in structural explanation.

The present paper, inter alia, contains additional structural determinations via ^{183}W NMR, but its main thrusts are (1) discussion and substantiation of the origins of ^{183}W NMR chemical shifts, (2) consequent correction of published interpretations and assignments of ^{183}W NMR bands[4] in two major categories of complexes, as examples, and (3) demonstration of the very promising structural tool of the ^{183}W nuclei's interactions with atoms having appropriate quadrupolar nuclei, when the latter atoms are structurally adjacent, in the complexes, to those WO$_n$

polyhedra that produce given bands. These interactions make band assignments possible, and when coupled with the ability to substitute many octahedrally coordinated elements for particular W atoms in polytungstate structures, first demonstrated[5] in 1966 and subsequently greatly elaborated upon by a variety of authors,[6] they provide numerous probes of great potential power for structure determinations in polyanions. The signals from all of the W atoms that are structurally immediately adjacent to the appropriate substituted atom become easily identifiable. For example, when ^{51}V^{5+} is isomorphously substituted for one or more W^{6+} atoms in a polytungstate structure (a common and easy substitution), the NMR signals from all the immediately *adjacent* W atoms may be greatly broadened, often to the extent of nonobservability. It is shown how this effect, besides enabling assignment of various bands, can be combined with other data to provide clear-cut direct substantiation for theory of NMR chemical shifts for transition elements like W(VI).

Experimental Section

Spectroscopy. All NMR spectra were obtained on a Bruker WH/HFX-90 FT NMR spectrometer operating at a magnetic field of 2.114 T (90.02 MHz for protons) with 10-mm diameter sample tubes at room temperature. Internal deuterium lock signal at 13.82 MHz was provided by the D$_2$O solvent used for all samples. Interfaced with the WH/HFX-90 spectrometer was a Nicolet BNC-12 data system with a 24K 20-bit word Nicolet minicomputer using a variable bit (6–12) A/D converter, QPD detection, and a hard-wired multipulser. The spectrometer was equipped to observe all nuclei with magnetic resonances between 3.7 and 40 MHz. A preamplifier tuned to the tungsten frequency (3.75 MHz) was used throughout all ^{183}W NMR experiments.

Chemical shifts, which are negative toward higher fields, are given in ppm with respect to an external saturated Na$_2$WO$_4$ solution (ca. 2 M) in 99.7 atom % D$_2$O at 28 °C and pD 9.1. The ^{183}W resonance in this solution was 3 750 719.9 Hz in a field in which the trimethylsilyl protons of sodium (trimethylsilyl)propanesulfonate (TSP) in a 1.0% by weight solution (pD 7.5) of that solute in 99.7 atom % D$_2$O resonate at 90 023 150.0 Hz at 28 °C when a D$_2$O lock is used.

Since the magnitude of a 90° pulse length depends in part on characteristics of the individual spectrometer, a preliminary experiment was

(1) From portions of the Ph.D. Dissertation of R.A., Georgetown University, 1981, who is on leave from the Department of Chemistry, School of Pharmacy, University of Valencia, Spain.

(2) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267.

(3) Acerete, R.; Harmalker, S.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777.

(4) Gansow, O. A.; Ho, R. K. C.; Klemperer, W. G. *J. Organomet. Chem.* **1980**, *187*, C27.

(5) Baker, L. C. W.; et al. *J. Am. Chem. Soc.* **1966**, *88*, 2329; *Proc. Int. Conf. Coord. Chem., 9th* **1966**, 421.

(6) Weakley, T. J. R. *Struct. Bonding (Berlin)* **1974**, *18*, 131.

^{183}W NMR for Polytungstates. Explanation of Chemical Shifts

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Table I. ^{183}W NMR Chemical Shifts^a in D_2O Solutions and Lowest Energy Optical Absorption Maxima for α-12-Tungsto Heteropoly Complexes ("Keggin" Structures)

compound	molarity	pD^b	δ, ppm ± 0.16	λ_{max} for lowest energy UV absorption, nm $\pm 0.8^c$
$H_4[GeW_{12}O_{40}]$	0.3	1.6	-81.9	267.5
$H_6[ZnW_{12}O_{40}]$	0.3	1.4	-95.8	265.2
$H_3[PW_{12}O_{40}]$	0.4	1.5	-99.4 (d, 1.17 Hz)	264.5
$H_4[SiW_{12}O_{40}]$	0.35	1.5	-103.8	262.9
$Na_6[H_2W_{12}O_{40}]$	0.15	0.4	-113.0	261.1
$Na_6[D_2W_{12}O_{40}]$	0.15	5.4	-120.0	259.6
$H_5[BW_{12}O_{40}]$	0.1	1.5	-130.8	257.1

^{a} Relative to external saturated Na_2WO_4 solution in D_2O (see text). ^{b} pD adjusted with DCl. ^{c} Obtained by deconvolution from charge-transfer tail.

used to obtain an approximate value. A pair of magnetically active nuclei (^{14}N and ^{81}Br) was selected for which the magnetogyric ratio was the same as that for ^{183}W and ^2D. Therefore, when the magnetic field was locked on the ^{81}Br resonance in a saturated solution of NH_4Br at 13.82 MHz by lowering the magnetic field to 1.236 T, the ^{14}N resonated at 3 795 194 Hz, which is very close to the frequency for ^{183}W when the field is locked on ^2D at 2.114 T. The ^{14}N data indicated a 90° pulse of 20 μs. The 90° pulse for ^{183}W was then accurately determined, from measurements on a 0.8 M solution of α-12-tungstosilicic acid in D_2O to be 17.5 μs using repetition times of 3.411 and 6.823 s.

For all subsequent spectra approximately 90° pulses (pulse length 17.5 μs) were used. This maximized signal intensity in contrast to the customary faster accumulation using a less than 90° pulse. The added time required for use of 90° pulses was not disadvantageous since long collection times were needed anyway to increase the resolution and minimize chances for line truncation.

Owing to the extreme narrowness of the ^{183}W NMR lines, spectra often contain bands that are incompletely defined in terms of data points. Care must be taken because this can result in truncation of the observed resonance signal and considerable reduction in the apparent intensity. For example, such truncation can be the main source of error in the determination of P–O–W coupling constants.

The typical acquisition time used was 3.411 s, usually without any added delay in the repetition time between pulses. Delay times of 2–10 times the dwell time (the time required to obtain one data point) were applied after each pulse to reduce the intensity of the ring-out signal that frequently appeared.

As a control, a 0.8 M solution of α-12-tungstosilicic acid was measured before each experiment. That solution required an accumulation time of only 10 min in order to obtain a good ^{183}W NMR spectrum.

Typical spectra involved accumulation of 15 000–25 000 pulses, requiring 14–24 h. For sparingly soluble compounds or spectra with many lines, accumulations lasting 3 days were required.

Ultraviolet and visible spectra were recorded on a Cary-14 spectrophotometer, and IR spectra were recorded on a Perkin-Elmer Model 457 grating instrument using samples in KBr disks.

Preparation and Identification of Compounds. The syntheses and purifications used for most of the heteropolytungstates studied were as reported previously.[7-13] The only exceptions are the preparations described in the next paragraph. All samples were identified in the solid state by their IR spectra, which agreed with the spectra found previously for the same compounds[14-18] in all cases except those of the V compounds,
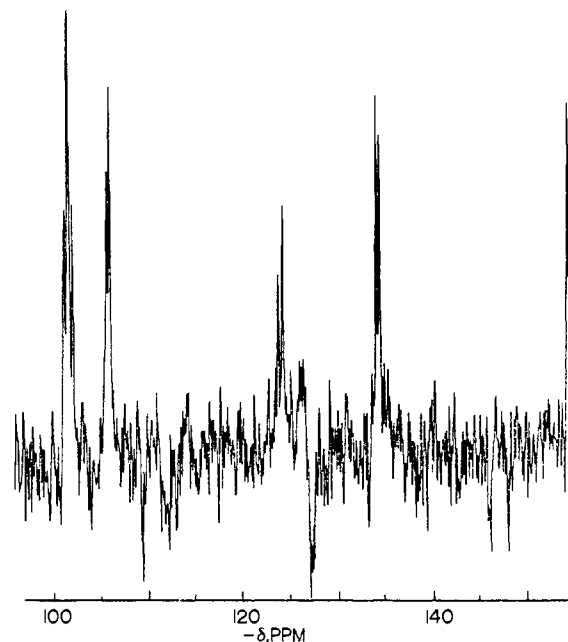

Figure 1. ^{183}W NMR spectrum of $[PW_{11}O_{39}]^{7-}$. The ionic strength of the solution has been increased by addition of $LiClO_4$ (ca. 0.5 M).
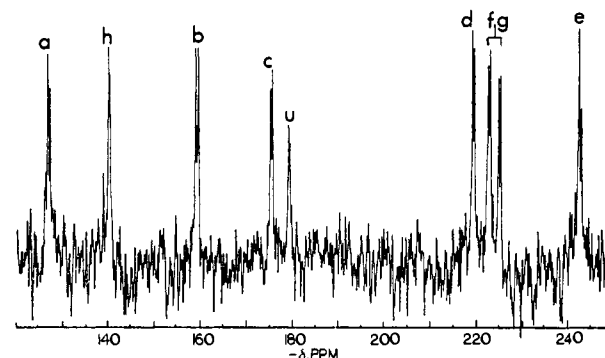
Figure 2. ^{183}W NMR spectrum of α_2-$[P_2W_{17}O_{61}]^{10-}$. The peaks are labeled with letters corresponding to the W's to which they are assigned, as identified in the structure shown in Figure 6.

for which no earlier spectra were reported. In addition, for comparison purposes, ^{31}P and ^{11}B NMR spectra of D_2O solutions were obtained for previously studied P and B compounds. The observed chemical shifts agreed with those reported previously.[19-21]

11-Tungstosilicate was prepared in D_2O solution from a 0.8 M solution of α-12-tungstosilicic acid by carefully adding $NaHCO_3$ until the pD increased to 8.4. Analogously, 11-tungstophosphate was prepared in D_2O solution from the "parent" compound, α-12-tungstophosphoric acid (ca. 0.6 M), by slow addition, with constant stirring, of enough Li_2CO_3 to raise the pD to 4.9. Similarly, the D_2O solution of α_2-$[P_2W_{17}O_{61}]^{10-}$ was prepared from a 0.6 M solution of its "parent", α-$Na_6[P_2W_{18}O_{62}]$, by increasing the pD to 5.1 by careful addition of $NaHCO_3$. α_2-$[P_2W_{17}VO_{62}]^{7-}$, α-$[SiW_{11}VO_{40}]^{5-}$, and α-$[PW_{11}VO_{40}]^{4-}$ were prepared by adding stoichiometric amounts of $NaVO_3$ to hot solutions (ca. 80 °C) containing purified α_2-$[P_2W_{17}O_{61}]^{10-}$, α-$[SiW_{11}O_{39}]^{8-}$, and α-$[PW_{11}O_{39}]^{7-}$, respectively. The orange solution of α_2-$[P_2W_{17}VO_{62}]^{7-}$, after addition of K^+ ions, deposited, upon cooling, yellow-orange crystals of the potassium salt, which was redissolved and converted to the lithium salt by a sulfonic acid type cation-exchange resin (Dowex-50) regenerated in the Li form and washed according to procedures described previously.[22]

(7) Schoenfeld, B.; Glemser, O. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1975, 30b, 827.

(8) Wexell, D. R. Ph.D. Dissertation, Georgetown University, 1972.

(9) Wu, H. J. Biol. Chem. 1920, 43, 189.

(10) Motorkina, R. K. Russ. J. Inorg. Chem. (Engl. Transl.) 1957, 2, 142.

(11) Freedman, M. L. J. Am. Chem. Soc. 1959, 81, 3834.

(12) Brown, D. H. J. Chem. Soc. 1958, 2597.

(13) Souchay, P. "Ions Mineraux Condensés"; Masson et Cie: Paris, 1969; p 106 ff.

(14) Rocchioccioli-Deltcheff, C.; Thouvenot, M. R. J. Chem. Res., Miniprint 1977, 549; C. R. Hebd. Seances Acad. Sci., Ser. C 1974, 278, 857.

(15) Rocchioccioli-Deltcheff, C.; Thouvenot, M. R.; Franck, R. Spectrochim. Acta, Part A 1976, 32A, 587.

(16) Termes, S. C. Ph.D. Dissertation, Georgetown University, 1976.

(17) Rocchioccioli-Deltcheff, C.; Thouvenot, M. R. Spectros. Lett. 1979, 12, 127.

(18) Nikitina, E. A.; Tsvetkov, N. A. Russ. J. Inorg. Chem. (Engl. Transl.) 1963, 8, 53.

(19) O'Donnell, S. E.; Pope, M. T. J. Chem. Soc., Dalton Trans. 1976, 2290.

(20) Massart, R.; Contant, R.; Fruchart, J.-M.; Ciabrini, J. P.; Fournier, M. Inorg. Chem. 1977, 16, 2916.

(21) Kazanskii, L. P.; Fedatov, M. A.; Spitsyn, V. I. Dokl. Akad. Nauk SSSR 1977, 234, 1376.

Table II. ^{183}W NMR Spectra of Some Heteropolytungstate Complexes in D_2O Solution

complex	counterion	molarity	resolution, Hz	$-\delta$ values, ppm^a ($^2J_{P-O-W}$ values, Hz)
$[SiW_{11}O_{39}]^{8-}$	Na^+	0.72	0.15	176.2 (2W); 143.2 (2W); 127.9 (2W); 121.3 (1W); 116.1 (2W); 100.9 (2W)
α-$[P_2W_{18}O_{62}]^{6-}$	Na^+	0.4	0.15	173.8 (d, 1.61, 12W); 128.1 (d, 1.17, 6W)
β-$[P_2W_{18}O_{62}]^{6-}$	Na^+	0.36	0.15	191.2 (d, 1.61, 6W); 171.1 (d, 1.61, 6W); 131.1 (d, 1.17, 3W); 111.6 (d, 1.32, 3W)
α_2-$[P_2W_{17}O_{61}]^{10-}$	Na^+	0.6	0.07	242.3 (d, 1.19, 2W); 225.0 (d, 1.69, 2W); 222.7 (d, 1.76, 2W); 218.9 (d, 1.54, 2W); 179.6 (d, 0.95, 1W); 175.8 (d, 1.76, 2W); 159.6 (d, 2.20, 2W); 140.8 (d, 1.03, 2W); 127.9 (d, 1.76, 2W)
α_2-$[P_2W_{17}VO_{62}]^{7-}$	Li^+	0.46	0.15	244.8 (d, 2.05, 2W); 225.4 (d, 1.76, 2W); 221.6 (d, 1.61, 2W); 220.0 (d, 1.61, 2W); 184.4 (d, 1.32, 1W); 182.5 (d, 1.61, 2W); 142.0 (d, 1.17, 2W)
$[PW_{11}O_{39}]^{7-}$	Li^+	0.51	0.29	153.5 (d, 1.17, 2W); 133.6 (d, 1.17, 2W); 122.9 (d, 1.76, 1W); 105.1 (d, 1.17, 2W); 100.9 (d, 2.05, 4W)
$[PW_{11}O_{39}]^{7-}$	Li^+	0.51^b	0.15	154.5 (d, 1.20, 2W); 134.5 (d, 1.37, 2W); 124.2 (d, 1.71, 1W); 106.3 (d, 1.20, 2W); 102.4 (d, 1.54, 2W); 102.0 (d, 1.54, 2W)

^{a} Relative to (upfield of) external saturated Na_2WO_4 solution in D_2O (see text). ^{b} Solution simultaneously 0.5 M with respect to $LiClO_4$.
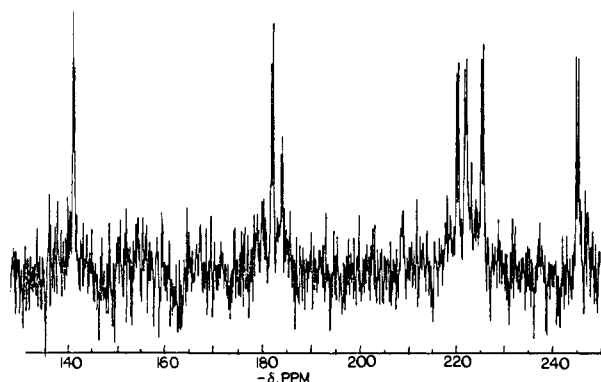

Figure 3. ^{183}W NMR spectrum of α_2-$[P_2W_{17}VO_{62}]^{7-}$.

The resulting solution was evaporated to obtain crystals of the lithium salt. 12-Tungstodeuterate was prepared in solution by adjusting the pD and allowing metatungstate to stand in D_2O for many times the half-time of exchange, as indicated by ^1H NMR.[23]

Results

Experimental results are summarized in Tables I and II. Each of the α-12-tungstates ("Keggin" structures) gave a spectrum consisting of a single sharp ($\Delta\nu_{1/2} \simeq$ 0.2–0.4 Hz) resonance, except for α-$[PW_{12}O_{40}]^{3-}$. All the ^{183}W NMR spectra of tungstophosphate derivatives studied are made up of very narrow ($\Delta\nu_{1/2} \simeq$ 0.2–0.3 Hz) base-line-resolved doublets, in which the splittings originate from the two-bond P–O–W couplings.[3]

The ^{183}W NMR spectra of α-$[SiW_{11}O_{39}]^{8-}$ and of α- and β-$[P_2W_{18}O_{62}]^{6-}$ appeared in our earlier papers,[2,3] and those of α-$[PW_{11}O_{39}]^{7-}$, α_2-$[P_2W_{17}O_{61}]^{10-}$, and α_2-$[P_2W_{17}V^{5+}O_{62}]^{7-}$ anions are given in Figures 1–3.

Discussion

The heteropoly-α-12-tungstate anions, $[X^{n+}W_{12}O_{40}]^{(8-n)-}$, are an isomorphous series having the well-known "Keggin" structure[6] (Figure 4) in which all 12 W atoms are structurally equivalent. Metatungstate, wherein $X^{n+} = H_2^{2+}$ (see caption of Figure 4), has the same tungsten–oxygen structure. The ^{183}W NMR spectrum for each complex therefore consists of a single sharp line (except when that line is split into a narrow doublet by coupling, as in the case of P–O–W coupling when $X^{n+} = P^{5+}$). Furthermore, the dimensions of the tungsten–oxygen cage are essentially identical in the various derivatives, and there is a sizeable cavity within such a cage that can accommodate centrally located $X^{n+}O_4$ tetrahedra of various sizes.[24-30] The ^{183}W NMR
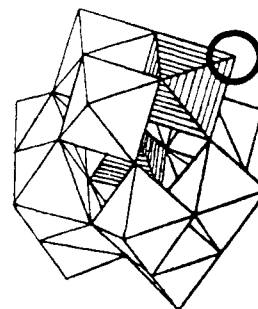
(22) Baker, L. C. W.; Loev, B.; McCutcheon, T. P. *J. Am. Chem. Soc.* **1950**, *72*, 2374.
(23) Landis, A. Ph.D. Dissertation, Georgetown University, 1977.
(24) Baker, L. C. W. In "Advances in the Chemistry of the Coordination Compounds"; Kirschner, S., Ed.; Macmillan: New York, 1961; p 608 ff.
(25) Razavi, H. Ph.D. Dissertation, Georgetown University, 1977.
(26) Smith, P. M. Ph.D. Dissertation, Georgetown University, 1972.
(27) D'Amour, H.; Allmann, R. A. *Z. Kristallogr.* **1976**, *143*, 1.

Figure 4. Structure of α-$[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (the "Keggin" structure) and of 11-tungstates derived therefrom. Each vertex of a polyhedron locates the center of a close-packed oxygen atom. The heteroatom X is generally at the center of the interior-hatched tetrahedron. (In the cases in which X^{n+} is H_2^{2+} or D_2^{2+}, the two H or D atoms probably lie off-center on opposite edges of the central tetrahedron at a given instant but are rapidly exchanging positions over the three pairs of opposite edges of that tetrahedron.) The ^{183}W NMR spectra confirm that the 11-tungsto complexes in solution have the same structure except each lacks one W (e.g., the hatched octahedron) and one of its O atoms (the unshared, circled one), yielding $[X^{n+}W_{11}O_{39}]^{(12-n)-}$. The dihetero-11-tungsto complexes, $[X^{n+}Z^{z+}W_{11}O_{40}]^{(12-n-z)-}$, have the Keggin structure but with a different octahedral element substituted for one of the 12 W's (e.g., V in the hatched octahedron).

chemical shifts for the derivatives wherein $X^{n+} = Zn^{2+}$, H_2^{2+}, D_2^{2+}, B^{3+}, Si^{4+}, Ge^{4+}, and P^{5+} are given in Table I.

The magnitude of the overall charge on the anion is controlled by the value of $n+$ in the formula. Accordingly, Gansow, Ho, and Klemperer,[4] using our early data,[2] have attempted to relate the ^{183}W NMR chemical shifts to the oxidation state of X on the basis that the overall anionic charge influences the electron density surrounding the W's and hence the nuclear shielding. Such a correlation shows no validity in the face of the data for the Zn^{2+} derivative (which is downfield from the P^{5+} and Si^{4+} complexes), the H_2^{2+} and D_2^{2+} complexes (which are downfield from the B^{3+} compound), and the Ge^{4+} anion (which is far downfield from the Si^{4+} complex as well as from all others). The nucleus is too deep and well shielded within a W atom for such inductive effects to be significant relative to the effects discussed below.

On the other hand, this series of complexes offers an unusual opportunity for a clear-cut substantiation of theoretical conclusions about the origins of NMR chemical shifts for transition elements. In sum, the nuclear shielding, and hence the chemical shift, depends upon two factors: (1) the anisotropy of the electric field around the transition-metal atom and (2) the availability of excited electronic states for mixing with the ground state. In the α-12-tungsto complexes, the anisotropy factor remains essentially constant, while the availability of excited-state mixing can be

(28) Allmann, R. A.; D'Amour, H. *Z. Kristallogr.* **1975**, *141*, 161.
(29) Feist, M.; Molchanov, V. M.; Kazanskii, L. P.; Torchenkova, E. A.; Spitsyn, V. I. *Zh. Neorg. Khim.* **1980**, *27*, 733.
(30) Standenberg, R. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3090.

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estimated from the optical spectra.

Theoretical Background. Ramsey's first- and second-order perturbation treatment of nuclear shielding[31] leads to an expression for the average shielding as the sum of two terms. The first is the same as Lamb's expression[32] for the diamagnetic shielding of single atoms while the second is the temperature-independent paramagnetic term, which arises from the lack of spherical symmetry of the electric potential.

While the diamagnetic term involves only the unperturbed ground state, the energies and wave functions of all the excited states participate in the temperature-independent paramagnetic term, which depends upon the unoccupied as well as the occupied molecular orbitals. The latter term involves the mixing of ground and excited states by the applied magnetic field.[33] The valence electrons of transition-metal atoms occupy p, d, and f orbitals with nonzero intrinsic angular moments, giving rise to large deviations from spherical symmetry. Therefore, transition-metal chemical shifts are most often dominated by the second-order paramagnetic contributions. Under the influence of the applied magnetic field, the molecular orbitals distort to allow virtual excitations or circulation of electrons by mixing-in of excited states,[34] thus providing some angular momentum to the ground state.

Within the frameworks of LCAO, MO, and valence bond theories, approximate methods were developed[33,35,36] to estimate total nuclear shielding. These methods have been extended by Jameson and Gutowsky[37] to include d- as well as p-orbital influence. They arrived at an expression for the paramagnetic term, of general applicability to spd hybridizations. The expression is essentially

$$\sigma^P = -\frac{2e^2h^2}{3m^2c^2\Delta E}[\langle 1/r^3 \rangle_p Pu + \langle 1/r^3 \rangle_d Du] \tag{1}$$

where Pu and Du represent respectively the "unbalance" of valence electrons in p and d orbitals centered on the atom. ΔE is the average energy of excitation to a state of the correct symmetry to be mixed with the ground state and is often given by the lowest energy UV–visible absorption maximum. $\langle 1/r^3 \rangle_{p,d}$ are the average values of $1/r^3$ for an electron in a p or d orbital of the atom.

Several attempts have been made to correlate experimental transition-metal nuclear shieldings with electronic excitation energies as measured from absorption spectra. An interpretation of chemical shifts developed by Griffith and Orgel[38,39] in terms of crystal field theory predicts a linear correlation between the nuclear shielding and the wavelength of the lowest frequency optical absorption maximum of octahedral complexes. That correlation has been relatively successful for studies of ^{51}Co NMR chemical shifts.[36,39,40] Deviations from linearity were ascribed to varying asymmetry of the complexes,[40] although this point has not been substantiated except by the success of the correlation presented below.

In each α-12-tungsto derivative, the lowest energy electronic transition appears as a small maximum on the side of the rapidly rising charge-transfer absorption. The position of the maximum of the electronic transition can be accurately determined by a single simple deconvolution. The wavelengths of the deconvoluted maxima are recorded in Table I. For reasons explained above, all terms in eq 1 are essentially constant in this series of compounds except for σ^P and ΔE. Chemical shifts (proportional to σ^P) are plotted against wavelengths since ΔE is in the denominator of eq 1.

(31) Ramsey, N. F. *Phys. Rev.* **1950**, *77*, 667; **1950**, *78*, 699.
(32) Lamb, W. *Phys. Rev.* **1941**, *60*, 817.
(33) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.
(34) Mason, J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 197.
(35) Karplus, M.; Das, T. P. *J. Chem. Phys.* **1961**, *34*, 1683.
(36) Pople, J. A. *J. Chem. Phys.* **1962**, *37*, 53.
(37) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714.
(38) Griffith, J. S.; Orgel, L. E. *Trans. Faraday Soc.* **1957**, *53*, 601.
(39) Freeman, R.; Murray, G. R.; Richards, R. E. *Proc. R. Soc. London, Ser. A* **1957**, *242*, 455.
(40) Juranić, N.; Ćelap, M. B.; Vučelić, D.; Malinar, M. J.; Radivojša, N. *J. Magn. Reson.* **1979**, *35*, 319.
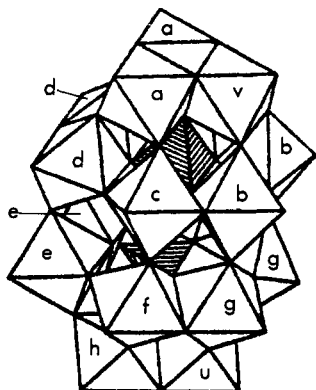

Figure 5. Plot of the ^{183}W NMR chemical shifts for α-$[X^{n+}W_{12}O_{40}]^{(8-n)-}$ complexes vs. the wavelengths of their lowest energy optical absorption maxima. The various X^{n+} heteroatoms are indicated on the diagram.

Figure 5 gives the impressive straight-line plot of ^{183}W NMR chemical shifts vs. wavelengths of lowest energy optical absorption maxima for all of the α-12-tungstates measured. There is no need to rationalize any deviations.

The diamagnetic shielding constant, σ^d, for W in $W^{6+}O_6$ octahedra may be evaluated from the intercept of Figure 5. A least-squares extrapolation (correlation factor 0.9966) yields $\sigma^d = -1304$ ppm. This value, or the slope in Figure 5 (4.60 ppm/nm), may be combined with the chemical shift and wavelength of the lowest energy optical absorption for a particular compound to obtain the $[\langle 1/r^3 \rangle_p Pu + \langle 1/r^3 \rangle_d Du]$ term (eq 1) for the anisotropy in all the α-12-tungstate complexes. Of course, σ^P for a given complex may also be evaluated from these data.

Effects of Ionic Strength, pD, and Concentration. Studies carried out with α-$[SiW_{12}O_{40}]^{4-}$, α-$[PW_{12}O_{40}]^{3-}$, and α-$[P_2W_{18}O_{62}]^{6-}$ showed that, within the ranges of chemical stability of the complexes, the ^{183}W NMR chemical shifts were not affected by the pD of the solution, but increases in ionic strength could change the chemical shifts upfield by several hertz (3.75 Hz = 1 ppm). As concentration of heteropoly electrolyte increases, ionic strength also increases, of course. The chemical shift caused by simply increasing concentration of measured species was merely that caused by the resultant increase in ionic strength, up to about $\mu = 2$, above which further increase in μ caused by added electrolyte gave a slightly greater effect than change in μ caused merely by increase in concentration of heteropoly compound. The small shift caused by increasing ionic strength is not precisely the same for each line in a spectrum.

Monohetero-11-tungstates. The ^{183}W NMR spectrum of α-$[SiW_{11}O_{39}]^{8-}$ was given in our first paper.[2] It consists of five separate 2W lines and one 1W line, thereby substantiating the postulate that the anion in solution consists of a Keggin structure from which one W atom and its unshared O atom have been removed.[2] The ^{183}W NMR spectrum of $[PW_{11}O_{39}]^{7-}$ (Figure 1) is very similar except that $^2J_{P-O-W}$ coupling causes each line to be a doublet. When this spectrum was taken in a solution of only moderate ionic strength, the two peaks that are farthest downfield overlapped, producing a single doublet of quadruple the area of the smallest peak. The small but nonuniform change of chemical shifts that had been observed upon change of ionic strength was therefore employed to resolve the large doublet into two equal-size doublets, overlapping to form a symmetrical triplet, as shown in Figure 1 (taken in a solution approximately 0.5 M in $LiClO_4$).

The wavelengths of the lowest energy optical absorptions for the monohetero-11-tungsto species differ from those of the corresponding α-12-tungsto anions. However, the straight line given in Figure 5 may be used to ascertain a predicted chemical shift corresponding to each such wavelength. Although each ^{183}W NMR spectrum for these complexes consists of six lines spread out over a range of parts per million, the center of area for the entire band system in a given ^{183}W NMR spectrum lies within about 20 ppm of the shift predicted from Figure 5 and the optical wavelength for that complex.

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Figure 6. The structure of α-$[P_2W_{18}O_{62}]^{6-}$ (the "Wells–Dawson" structure). Each vertex of a polyhedron locates the center of a close-packed O atom. The P atoms are at the centers of the interior (hatched) tetrahedra. Every octahedron contains a W atom. The α_2 isomer of $[P_2W_{17}O_{61}]^{10-}$ has a structure identical with that illustrated except that one W atom (labeled "v" in the figure) and its unshared O atom have been removed from the threefold W_3O_{13} cap on the top of the complex.[3] Many other octahedrally coordinated atoms can be substituted for particular W atoms. For example, α_2-$[P_2W_{17}VO_{62}]^{7-}$ has the structure illustrated except that a V^{5+} has replaced one W^{6+} in the threefold cap group. The structurally unique W in the 17-tungsto derivatives is labeled "u" in the figure. Each member of a pair of structurally equivalent W's in the 17-tungsto derivatives is designated by a given letter, identical for those two W's.

Discussion of line assignments in the 11-tungsto complexes will be given in terms of the results obtained for the α_2-$[P_2W_{17}O_{61}]^{10-}$ and α_2-$[P_2W_{17}VO_{62}]^{7-}$ species.

α- **and** β-$[P_2W_{18}O_{62}]^{6-}$, **Sensitivity of Coupling Constants.** The ^{183}W NMR spectra for α-$[P_2W_{18}O_{62}]^{6-}$, for its β isomer, and for α-$[PW_{12}O_{40}]^{3-}$ were given in our earlier communications.[2,3] Besides proving that the basis for the isomerism of the P_2W_{18} derivatives is a 60° rotation of one of the threefold W_3O_{13} "caps" of the complex (Figure 6), these spectra, and numerous subsequent duplicate ones, showed that the $^2J_{P-O-W}$ coupling constants for the narrow but base-line-resolved doublets accurately reflect very small differences in P–O–W distances (as small as 0.04 Å) obtained from accurate structural X-ray crystallography.[2]

α_2-$[P_2W_{17}O_{61}]^{10-}$, α_2-$[P_2W_{17}VO_{62}]^{7-}$, **and Assignment of Lines.** The ^{183}W NMR spectrum of α_2-$[P_2W_{17}O_{61}]^{10-}$ is shown in Figure 2, and the spectral data are given in Table II. This spectrum of nine doublets with area ratios 2:2:2:2:1:2:2:2:2 proves that α_2-$[P_2W_{17}O_{61}]^{10-}$ differs from its α-$[P_2W_{18}O_{62}]^{6-}$ parent by removal of one W atom (and its unshared oxygen) from one of the threefold W_3O_{13} caps of the complex[3] (Figure 6). The small peak must be assigned to the structurally unique W in the cap on the end of the complex opposite to the end from which the W removal occurred. Each of the other lines corresponds to a pair of structurally equivalent W's.

α_2-$[P_2W_{17}VO_{62}]^{7-}$ has the same structure as α_2-$[P_2W_{18}O_{62}]^{6-}$ except that a V^{5+} atom has been inserted in one of the W_3O_{13} caps[3] in place of a W, that is, into the same location as was vacant in α_2-$[P_2W_{17}O_{61}]^{10-}$. The ^{183}W NMR spectrum of this vanado-17-tungsto complex is shown in Figure 3, and the spectral data are given in Table II. The spectrum is basically similar to that of α_2-$[P_2W_{17}O_{61}]^{10-}$ except that the nuclear quadrupolar moment of ^{51}V has provided a mechanism for the rapid relaxation of the ^{183}W atoms in sites adjacent to it, thereby broadening the lines for those W's into the spectrum's background. Therefore, two of the 2W lines found in the spectrum of α_2-$[P_2W_{17}O_{61}]^{10-}$ are missing from the α_2-$[P_2W_{17}VO_{62}]^{7-}$ spectrum. (The spectrum was searched for 300 ppm on each side of the spectrum given in Figure 3.) Those missing lines correspond to the two cap W's adjacent to the V and the two belt W's adjacent to the V.

The ^{51}V NMR spectrum of $[W_5VO_{19}]^{3-}$ has been measured by Leparulo,[41] who found the $^2J_{V-O-W}$ to be 10 Hz for those edge-

and corner-sharing octahedra. To be efficient for spin–lattice relaxation of ^{183}W, the fluctuations produced by the quadrupolar ^{51}V nucleus on the magnetic field must be rapid relative to the coupling constant.[42-44] A ^{51}V NMR spectrum provides information on the lifetime of the excited states of that quadrupolar nucleus.[45] Leparulo[46] has found the line width to be 30 Hz at half-height for the single ^{51}V NMR signal in α_2-$[P_2W_{17}VO_{62}]^{7-}$. The Heisenberg principle allows the spin–lattice relaxation for vanadium to be calculated from

$$\Delta\nu_{1/2}{}^V \simeq 1/(\pi T_2) \qquad (2)$$

and

$$T_2{}^V = T_1{}^V = 1/(\pi\Delta\nu_{1/2}{}^V) = 1.06 \times 10^{-2}\ s \qquad (3)$$

The spin–lattice relaxation time of ^{51}V is thus much shorter than the reciprocal of the $^2J_{V-O-W}$. Under such conditions the relaxation rate for the coupled ^{183}W nuclei is given by[42-44]

$$1/T_2{}^W = $$
$$(4/3)\pi^2(^2J_{V-O-W})^2S(S+1)[T^V + T^V/(1 + 4\pi^2\Delta\omega^2(T^V)^2)] \qquad (4)$$

and for $^2J_{V-O-W} = 10$ Hz and $T^V = 1.06 \times 10^{-2}$ s, the expression gives $1/T_2{}^W = 220$ s^{-1}. This analysis predicts that spin–spin coupling of ^{51}V with ^{183}W in neighboring sites in α_2-$[P_2W_{17}VO_{62}]^{7-}$ would produce resonances for the coupled ^{183}W atoms having a width at half-height of

$$\Delta\nu_{1/2}{}^W \simeq 1/(\pi T_2{}^W) = 70\ Hz$$

That is, the ^{51}V–O–^{183}W coupling produces over a hundredfold broadening of the ^{183}W NMR signal, which results in the practical loss of those resonances in this compound's spectrum.

The assignment of the single 1W NMR line in the spectrum of α_2-$[P_2W_{17}O_{61}]^{10-}$ and the identification proposed above of the two 2W lines for W's adjacent to its vacant W site, via the latter lines' elimination in the spectrum of α_2-$[P_2W_{17}VO_{62}]^{7-}$, allow us to propose assignments for all the lines in the spectrum (Figure 2) by incorporating with that information the P–O–W coupling constants and chemical shifts observed for α_2-$[P_2W_{17}O_{61}]^{10-}$, α_2-$[P_2W_{17}VO_{62}]^{7-}$, α-$[PW_{12}O_{40}]^{3-}$, α-$[P_2W_{18}O_{62}]^{6-}$, and β-$[P_2W_{18}O_{62}]^{6-}$. In the latter two spectra the lines for belt and cap W's are identified by their areas.[2,3] Confidence in the proposed assignment of lines is especially high because it is consistent with and supported by each of the numerous lines of interlocking evidence in all of these spectra. The assignment in turn facilitates understanding of the other ^{183}W spectra.

We conclude that the magnitudes of the chemical shifts in the 17-tungsto and 11-tungsto species result from two factors. (1) The first is the observed lowering of the wavelength of the lowest optical absorption for each complex that lacks one W, as contrasted with its 18-tungsto or 12-tungsto parent. This decrease of the availability of the excited state tends, as expected, to produce a distinct upfield shift for all the W's. (2) Superimposed on that effect is a downfield shift of approximately comparable magnitude for those W's that undergo an increase in electronic anisotropy owing to the distortion introduced by removal of a nearby W atom. The net effect is minimal net shifts for those W's near the vacancy and large upfield shifts for the W's that are far from the vacancy. This is substantiated by the fact that those W signals which shifted little when the vacancy was formed are the signals which get broadened or eliminated when V^{5+} is substituted into the vacancy.

Thus we have the novel, although not really paradoxical, cases of spectra wherein the changes of chemical shifts for atoms far

(41) Leparulo, M. A. M.S. Thesis, Georgetown University, 1978.

(42) Abragam, A. "The Principles of Nuclear Magnetism"; Oxford University Press: London, 1961; p 306 ff.

(43) Becker, E. D. In "Nuclear Magnetic Resonance of Nuclei Other Than Protons"; Axenrod, T., Webb, G. A., Eds.; Wiley: New York, 1974; p 1 ff.

(44) Shaw, D. "Fourier Transform N.M.R. Spectroscopy"; Elsevier: New York, 1976; p 311 ff.

(45) Balimann, G.; Pregosin, P. S. *J. Magn. Reson.* **1977**, *26*, 283.

(46) Leparulo, M. A., private communication, 1981.

from the perturbed sites are large, while the changes of chemical shifts for atoms near the perturbing sites are minimal.

It is to be expected that when the W atom is removed from one cap of the α-$[P_2W_{18}O_{62}]^{6-}$, the P^{5+} atom near that cap will move a little closer to the vacant site, which is less positive than when it was occupied by a W in the parent ion. This movement is supported by increase in the P–O–W coupling constants for the W's near the vacancy (identified by the disappearance of their signals when V^{5+} is inserted in the vacancy) and by decrease in P–O–W coupling constants for those belt W's away from which the P^{5+} moves. Although they did not consider it, that shift in P position is also supported by the ^{31}P NMR chemical shifts observed by Massart et al.[20] and Contant et al.[47]

The 1W doublet at −179.6 ppm assigned above to the structurally unique W (which is in the intact cap) has $^2J_{P-O-W} = 0.95 \pm 0.07$ Hz. The only comparably low $^2J_{P-O-W}$ value is 1.03 ± 0.07 Hz for the 2W line at −140.8 ppm. Those constants are smaller than but close to the low 1.17-Hz values found for all the cap W's in α-$[P_2W_{18}O_{62}]^{6-}$, for all the W's in α-$[PW_{12}O_{40}]^{3-}$, and for the W's in the unrotated cap[3] of β-$[P_2W_{18}O_{62}]^{6-}$. Belt W's in these unsubstituted compounds all have much larger P–O–W coupling constants, close to 1.61 Hz. Therefore, the 2W line at −140.8 ppm is assigned to the other two W's in the lower (intact) cap.

As the P^{5+} adjacent to the vacancy moves closer to the less positive vacancy (or V^{5+}), in comparison to that P's position in the 18-tungsto complex, the other P^{5+} would be expected to be displaced very slightly away from its intact cap and toward the side of its belt farthest away from the vacancy. This movement is reflected in the relative sizes of the P–O–W coupling constants given in the preceding paragraph for the three W's in the intact cap and in their slight but real reduction from the usual cap $^2J_{P-O-W}$ values. It will also be noted that the signals for the W's in the intact cap have all been shifted markedly upfield from their positions in the 18-tungsto parent. This coincides with the remoteness of those W's from the vacancy, in accordance with the general interpretation explained above.

The two 2W bands at −127.9 ppm ($^2J_{P-O-W} = 1.76$ Hz) and −159.6 ppm ($^2J_{P-O-W} = 2.20$ Hz) are the ones that are removed when V^{5+} is substituted into the vacancy. On the basis of the coupling constants, the former is assigned to the two remaining cap W's next to the vacancy and the latter to the two belt W's next to the vacancy. The P–O–W coupling constants for W's in undistorted caps are 1.17 Hz, and for undistorted belt W's they are ∼1.61 Hz. The increases in $^2J_{P-O-W}$ values in the 17-tungsto complex result from the movement of the adjacent P^{5+} described above. It will be noted that the chemical shift for the first of these lines is essentially the same as in the parent complex owing to the compensating factors of increased electronic anisotropy and lower availability of the excited state, as explained above. The line at −159.6 ppm, however, is the only signal that shifted downfield (by a modest amount) when the adjacent vacancy was introduced, indicating a slight predominance of the effect of increased electronic anisotropy.

The 2W line at −175.8 ppm ($^2J_{P-O-W} = 1.76$ Hz) is assigned to the middle W's of the upper belt (the W_c's in Figure 6). The coupling constant is close to that of typical belt W's in the parent complexes, and its chemical shift was only 2 ppm upfield from its position in the 18-tungsto parent (indicating reasonable closeness to the distorting vacancy). Further, of the lines that were not eradicated by the substitution of V^{5+} into the vacancy, this is the only 2W peak for which the chemical shift differs substantially in the two 17-tungsto complexes, as would be expected from its position relatively near the vacancy (or V^{5+}) site.

The remaining four 2W lines were all shifted far upfield by the introduction of the vacancy (or V^{5+}) and hence are distant from that distorting site and therefore subject primarily to the effect of lowered availability of excited states without the counterbalancing effects of increased paramagnetic anisotropy. Further substantiation of their remoteness from the vacancy (or V^{5+}) is

the fact that their chemical shifts are almost identical in the two 17-tungsto complexes (with and without V^{5+}). The line shifted most, at −242.3 ppm, has $^2J_{P-O-W} = 1.91$ Hz. It is assigned to the two lower belt W_e's (Figure 6) that are farthest from the vacancy. Its distinctly increased coupling constant, over that typical of belt W's in the parent complex, reflects the increased proximity of the adjacent P, as explained above. Consistent with all these ideas, we can assign the 2W line at −218.9 ppm ($^2J_{P-O-W} = 1.54$ Hz) to the pair of W's in the upper belt that are farthest from the vacancy. The lowering of its coupling constant from the usual value for a belt W in the parent complexes follows from the shift of the adjacent P atom away from that pair of W's. The remaining two 2W lines are close in chemical shifts (−222.7 and −225.0 ppm) and close in coupling constants (1.76 and 1.69 Hz, respectively). They belong to the remaining two pairs of W's in the lower belt (W_f's and W_g's in Figure 6). It is not possible to distinguish them with a confidence comparable to the other assignments. On the basis of their coupling constants and the slight shift of the adjacent P atom, which may be regarded as reasonably established by the other observations, the line at −222.7 ppm might be assigned to the two W_f's and the line at −225.0 ppm to the two W_g's.

11-Tungsto Derivatives. We can now return to the consideration, started above, of the $[SiW_{11}O_{39}]^{8-}$ ^{183}W NMR spectrum[2] and that of its isomorph $[PW_{11}O_{39}]^{7-}$ (Figure 1) and of other 11-tungsto heteropoly species. Here again, the wavelength of the lowest optical absorption is lower for each 11-tungsto species than for its 12-tungsto parent, producing a general upfield shift tendency for all the lines; here again, the increased electronic anisotropy of the W's near the vacancy (or near the V^{5+} substitution) produces a counterbalancing downfield shift for the resonances of those W's. In complete accordance with the interpretation explained in the previous section, it is the two most downfield 2W lines of the spectrum of $[SiW_{11}O_{39}]^{8-}$ or of $[PW_{11}O_{39}]^{7-}$ that get broadened (but not eliminated in these cases) by the introduction of V^{5+} into the respective W vacancies. It is also those two lines that experience moderately large chemical shifts when the V^{5+} is introduced, while the other lines remain relatively fixed. It is also those two lines that show the most increase in $^2J_{P-O-W}$ (from ∼1.17 Hz in α-$[PW_{12}O_{40}]^{3-}$ to 2.05 Hz in $[PW_{11}O_{39}]^{7-}$), corresponding to a movement of the P^{5+} toward the less positive vacancy. The two lowest field lines may, on all these grounds, be confidently assigned to the two pairs of W's nearest to the vacancy, and the smallest line must, of course, be assigned to the structurally unique W. The variations in the other coupling constants are small and do not permit the origins of the other three lines to be confidently assigned.

Gansow, Ho, and Klemperer[4] reported the ^{183}W NMR spectrum of α-$[\eta^5\text{-}C_5H_5Ti(PW_{11}O_{39})]^{4-}$ taken in pure CD_3CN and in a CD_3CN plus $(CH_3)_2NCHO$ mixture. It is basically similar to the 11-tungsto spectra just discussed. That 11-tungsto complex has the same structure as the heteropoly-11-tungstates considered above except that Ti has been substituted into the vacancy and the Ti is also attached to the cyclopentadiene moiety. Unfortunately, their spectrum lacked sufficient resolution to detect the small variations in coupling constants. Those authors assigned the lines in the spectrum on the basis of a postulated trans conveyance of negative charge through the octahedra adjacent to the Ti and thence, in attenuated degree, via further trans conveyance through the next octahedra, and so on. Their assignment is based completely on relative shieldings of W's by negative charges, governed by the postulated transmissions of charge. That simple view is not pertinent for NMR spectra of this type, as the discussion in the present paper shows. It led those authors to completely incorrect assignments wherein the most upfield lines, instead of those furthest downfield, were ascribed to the resonances of the W's nearest the Ti.

(47) Contant, R.; Ciabrini, J.-P. *J. Chem. Res., Synop.* **1977**, 222; *J. Chem. Res., Miniprint* **1977**, 2601.

Determination of the Onset of the Dezincification of α-Brass Using X-ray Photoelectron (ESCA) Spectroscopy

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Abstract: The initial effect observed during the dezincification of air-passivated α-brass in simulated seawater is the migration of Zn^{2+} from the alloy, through the passivation layers, to form an overlayer of ZnO. Subsequent layer thickening, selective oxide dissolution, and island formation are also documented. A general mechanism is proposed.

Dezincification of Cu–Zn brasses is a classic corrosion problem[1] for which the mechanism is still not entirely understood.[2] Extensive studies during the early part of this century indicated two possible mechanisms for the process:[2] (1) the preferential migration of zinc to the surface of the brass with its subsequent removal by fluid flow[3] and (2) the uniform dissolution of the alloy into the fluid with subsequent selective precipitation of Cu onto the alloy surface as a porous (spongy) Cu, leaving the Zn behind in solution.[4] The present consensus appears to favor mechanism 2.[5] However, it has been proposed that both may sometimes occur in sequential fashion.[1] In any case, the area of the brass affected by dezincification is known to exhibit a loss of Zn and the retained Cu, a spongy morphology. The surface in this region often exhibits a white appearance,[1,2] as opposed to the golden yellow characteristic of the unaffected brass. The former occurs primarily when dezincification is achieved in saltwater, and the color change has been attributed to the formation of Cu_2Cl_2.[2] In order to elucidate the mechanism for this process, we studied the onset of the dezincification of α-brasses (percent Cu >70) by using X-ray photoelectron spectroscopy.

Experimental Section

The process was activated by immersing coupons of thin α-brass foils into a simulated seawater solution (3% NaCl by weight), hereafter referred to as "the salt solution". The preimmersion composition of the high-purity foil was determined by X-ray microprobe to be Cu ≃ 74.5% and Zn 24.5 ± 1.0%. Prior to immersion, the foils were permitted to experience "natural passivation" in clean air, i.e., the natural conversion (tarnishing) of the surface Cu(0) and Zn(0) to a thin film of the corresponding oxides (and hydroxides).[6] The details of this natural oxidation have been documented and published elsewhere.[7] Figure 1a demonstrates the layering structure typical of that resulting from the exposure of the α-brasses in question to ambient air. This preliminary process was permitted because "real"-use situations for brass (e.g., condenser tubes, etc.) will invariably expose the passivated rather than the zero-valent surface to the onset of dezincification. The existence of an outer surface rich in copper is a particularly important feature of passivation. This passivated surface should affect the temporal aspects of the onset of dezincification.

Individual coupons of the brass were removed from the salt solution at periodic intervals, rinsed clean (to "fix" the process), dried, examined in an optical microscope, and inserted into the vacuum chamber of the Hewlett-Packard 5950A ESCA X-ray photoelectron spectrometer. The entire transfer process (solution to 1 × 10⁻⁹ torr vacuum) was accomplished in a few minutes—a relatively short period compared to the hours of immersion needed to affect significant changes. The present study was accomplished mainly in a static salt solution at 25 ± 2 °C. ESCA profiles were obtained of the coupons during the study (outer dezincified surface to the bulk of the zero-valent alloy) by ion milling using high purity argon. The potential ill effects of ion etching have been noted[6b,7,8] and monitored in this study. No problems significant enough to endanger the general conclusions of this study were found. The details of this aspect of the study will be presented elsewhere.[9a] The fortuitous similarity in the atomic masses of Cu and Zn assisted in this aspect of the study.

The pH of the immersion solution was monitored during these experiments and found to remain slightly acidic, pH 6.0 ± 0.5, throughout. The pH will, of course, affect the mobility and type of ions formed in solution and also at the interfaces, particularly if the principal process is electrochemical. Under the latter circumstances, it would be instructive to try to identify the parts of the metal surfaces functioning as the electrodes and also to monitor the distribution of products under various pH settings, since extreme variations could dramatically effect the reported results. These feature are left for future studies.

The results to be described were generated from ESCA observations of selected 5 × 1 mm regions on the surfaces of the aforementioned polycrystalline alloy foils. The results were thus selective and yet deemed to represent a *statistical average* of those realized by the *total* alloy surface. This assumption is based, in part, upon the microscopic observation that the grain size of the alloys employed was found to be extremely small (<4 μm) and relatively uniform. The materials were also periodically examined by optical microscopy (during treatment), and no preferential sites of reaction were detected in the area of observation. Thus, it should be realized that any preferential metallurgical events (e.g., grain boundary migration vs. mobility inside of the grains) that no doubt occur are undetected in this study *but* should be uniformly weighted in the results by the relatively large field of observation.[7] For this reason,

(1) Evans, U. R. "The Corrosion and Oxidation of Metals"; Arnold: London, 1960; pp 471–80.

(2) Gilbert, P. T. "Corrosion"; Shreir, L. L., Ed.; Butterworths: London, 1976; Vol. 1.

(3) Pickering, H. *J. Electrochem. Soc.* **1970**, *117*, 8.

(4) Lucy, V. F. *Br. Corros.* **1965** *I*, 9; **1965** *I*, 52.

(5) Boyer, H. E., Ed. "Metals Handbook", 8th ed.; American Society for Metals: Metals Park, OH, 1975; Vol. 10, pp 175–77.

(6) (a) Barr, T. L. *J. Vac. Sci. Technol.* **1977**, *14*, 660. Barr, T. L. "Quantitative Surface Analysis of Materials"; McIntyre, N. S., Ed., ASTM: Philadelphia, PA, 1978; STP 643, pp 83–104. (b) Barr, T. L. *J. Phys. Chem.* **1978**, *82*, 1801.

(7) Barr, T. L.; Hackenberg, J. J., *Appl. Surf. Sci.*, in press.

(8) Greene, J. E.; Klinger, R. E.; Barr, T. L.; Welsh, L. B. *Chem. Phys. Lett.* **1979**, *62*, 46.

(9) (a) Barr, T. L., to be submitted for publication. (b) The term "surface" refers here to the outer layers of a solid with thickness of ~30 Å, i.e., the approximate "observation depth" of the ESCA.

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