Assignment of Multiline Tungsten-183 NMR Spectra of Diamagnetic Polyoxotungstates from Intensity Patterns

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Measurement of relative integrated intensities and peak heights of multiline one-dimensional ^{183}W NMR spectra of diamagnetic polyoxotungstates can result in complete or partial assignment of chemical shifts, even when ^{183}W−^{183}W spin-coupled satellites are not detectable or well-resolved. The intensity of the center peak of each signal is diminished according to the number and type (corner- vs edge-sharing of WO_6 octahedra) of potential spin-couplings. Application of the method is exemplified by analysis of spectra of α-$[XW_{11}O_{39}]^{n-}$ and derivatives, α_2-$[P_2W_{17}O_{61}]^{10-}$, and $[As_4W_{40}O_{140}]^{28-}$. Intensity patterns of the six-line spectra of the β_1 and β_3 isomers of $[XW_{11}O_{39}]^{n-}$ are sufficiently different to allow identification.

Introduction

Polyoxometalates represent a greatly diverse class of compounds, recent interest in which is derived from their applications as catalysts and as specific agents in analytical chemistry and medicine.[1,2] Unambiguous identification and elucidation of polyoxotungstate structures, keys to the investigation of their activity and electronic structures, have mainly been achieved by X-ray crystallography and ^{183}W NMR spectroscopy. The latter method is of special importance since diffraction-quality nondisordered crystals cannot always be obtained and because many of the applications of polyoxotungstates occur in solution.

The high symmetry of many polyoxotungstate structures results in ^{183}W NMR spectra with one or two lines for which assignment is trivial, but complexes of lower symmetry, especially lacunary anions and their derivatives, yield multiline spectra.[3] Analysis of the latter depended upon observation of $^{2}J_{W-O-W}$ satellites (∼7% of the peak) and elucidation of tungsten−tungsten connectivities from 1D- and 2D-COSY and 2D-INADEQUATE techniques.[4−6] Accumulation of such spectra requires concentrated solutions (not always achievable) and long acquisition times. Cation exchange of poorly soluble salts to achieve higher anion concentrations has been shown to lead to structural changes[7] or at least to changes in chemical shifts.[5a]

In this paper we show that, for 1D ^{183}W NMR spectra of diamagnetic polyoxotungstates recorded under conditions where ^{183}W−^{183}W satellites are not clearly observable or resolved from the central peak, the relative peak intensities and heights provide much more information regarding peak assignment than seems to have been recognized previously. In favorable cases, it also becomes possible to discriminate between isomers.

Experimental Section

The potassium salts of α-$[PW_{11}O_{39}]^{7-}$ (**1**) and α-$[SiW_{11}O_{39}]^{8-}$ (**2**) and a lithium salt of bis(acetato)(11-tungstophosphato)dirhodate(II), $Rh_2(O_2CCH_3)_2PW_{11}O_{39}{}^{5-}$ (**3**), were prepared using literature methods.[8−10] Spectra were recorded in D_2O, in 10 mm tubes, at room temperature, on a Bruker AM-300 NMR spectrometer (operating frequency 12.50 MHz), equipped with an ASPECT 3000 computer. The parameters were as follows: 45° flip angle, 3 s interpulse delay, spectrum width of 3500 Hz, 32K data points, and 7000−15 000 scans. After zero-filling to 64K, the final resolution was 0.11 Hz/pt. An acquisition time of 4.6 s together with the interpulse delay provided full relaxation of all the tungsten nuclei.[11]

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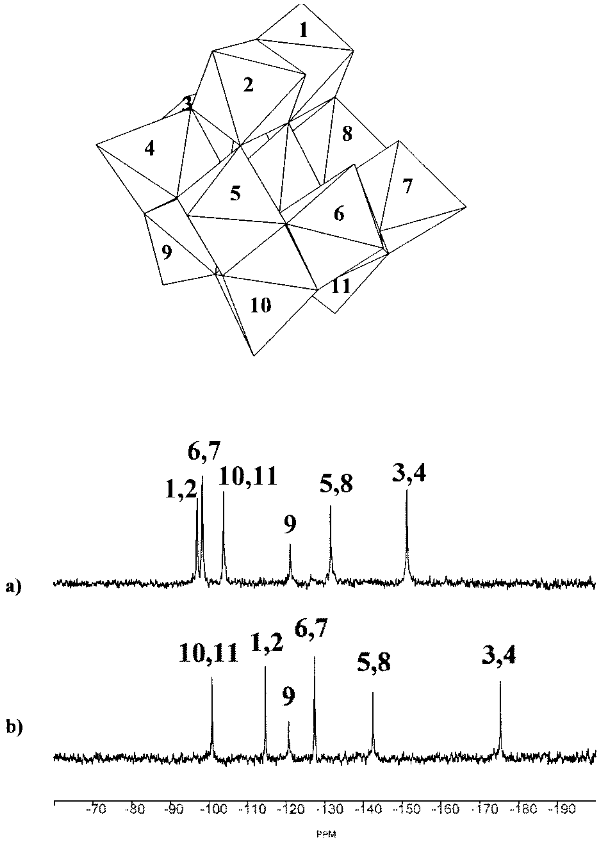

Figure 1. ^{183}W NMR spectra of 0.1 M solutions of (a) $K_7PW_{11}O_{39}$ in 5.0 M LiCl solution and (b) $K_8SiW_{11}O_{39}$ in 3 M NaCl solution. Assignments are in accordance with ref 5a.

Results and Discussion

A tungsten-183 NMR signal in diamagnetic heteropolyoxometalates is usually narrow,[3a] and it consists of a central line corresponding to ^{183}W atoms without any ^{183}W neighbors, "close" satellites from edge-shared WO_6 octahedra, and "distant" satellites from corner-shared octahedra. Due to secondary isotope shifting, the satellites are located asymmetrically around the central line. The magnitudes of $^2J_{W-O-W}$(edge) are usually in the range 4−7 Hz, while those of $^2J_{W-O-W}$(corner) are significantly larger (15−34 Hz),[4−6] with rare exceptions.[5c,6] In Keggin-structure-derived tungstophosphates, both the central line and the satellites exhibit $^2J_{W-O-P}$ values of ca. 1 Hz. Most heteropolytungstates possess elements of symmetry, giving rise to a number of tungstens with the same chemical shifts. Thus a mirror plane in the lacunary anion α-$[PW_{11}O_{39}]^{7-}$ results in a ^{183}W NMR spectrum with six signals. A unique W_9 (Figure 1) exhibits the smallest intensity, and five resonances with larger intensities correspond to the pairs of symmetrical isochronous tungstens.

However, as shown in Figure 1, the actually observed integral intensities of the tungsten signals are usually different even if they correspond to the same number of atoms. The spectra in Figure 1 are based on overnight accumulations of 0.1 M solutions of **1** and **2**, and under these conditions the tungsten satellites were not observable. The line assignments were made in accordance with the results obtained by Brévard et al.,[5a] who used 2D-COSY and 2D-INADEQUATE methods, high concentrations, 1.2 M $Li_7PW_{11}O_{39}$ and 0.8 M $Na_8SiW_{11}O_{39}$, and ca. 30 h spectral accumulation times. Relative integral intensities of the observed peaks are shown in Table 1 and reveal similarities for both species. This prompted us to exploit the possibility of using intensity variations for assignments of chemical shifts in the tungsten-183 NMR spectra of moderately concentrated solutions of heteropolytungstates.

Table 1. Chemical Shifts and Relative Integral Intensities of Observed Signals in ^{183}W NMR Spectra of 0.1 M Solutions of α-$[PW_{11}O_{39}]^{7-}$ (in 5 M LiCl) and α-$[SiW_{11}O_{39}]^{8-}$ (in 3 M NaCl)

	α-$[PW_{11}O_{39}]^{7-}$			α-$[SiW_{11}O_{39}]^{8-}$		
atom	δ (ppm)	integral intensity	no. of atoms	δ (ppm)	integral intensity	no. of atoms
$W_{1,2}$	−97.2	1.4	2	−114.9	1.4	2
$W_{3,4}$	−151.5	1.6	2	−175.6	1.6	2
$W_{5,8}$	−131.8	1.3	2	−142.8	1.5	2
$W_{6,7}$	−98.5	2.0	2	−127.7	2.0	2
W_9	−121.2	0.7	1	−121.0	0.7	1
$W_{10,11}$	−104.0	1.8	2	−101.1	1.7	2

Table 2. Numbers of Corner- and Edge-Sharings and Calculated Relative Intensities of Coalesced Peaks in ^{183}W NMR Spectrum of α-$[XW_{11}O_{39}]^{n-}$

atom	corner-sharings	edge-sharings	integral intensity	no. of atoms
$W_{1,2}$	2	0	1.49	2
$W_{3,4}$	2	1	1.49	2
$W_{5,8}$	2	2	1.49	2
$W_{6,7}$	0	2	2.00	2
W_9	2	2	0.75	1
$W_{10,11}$	1	2	1.71	2

Line Integral Intensities. Different tungsten atoms in polyoxoanions have different numbers of edge- and corner-sharing neighbors. Each $^2J_{W-O-W}$ coupling constant accounts for 14.27% of the overall signal, reflecting the probability of the presence of two such atoms in the molecule.[12] *As a result, the central peak intensity decreases proportionally to the number of* $^2J_{W-O-W}$*'s experienced by the tungsten atom* (eq 1). In tungstophosphates, the couplings to the phosphorus atom are also observed, but these are relatively small and do not change the tungsten intensity distribution to any noticeable extent. Therefore the intensity of the central line is, to first order

$$\text{central line integral intensity} = N_W(1 - 0.1427(N_{\text{corner}} + N_{\text{edge}})) \quad (1)$$

where N_W is the number of isochronous tungsten atoms of interest and N_{corner} and N_{edge} are the numbers of corner and edge $^2J_{W-O-W}$ coupling constants, respectively.

The small values of edge-sharing coupling constants in the ^{183}W NMR spectra of dilute solutions generate satellites that are hardly separable from the central line due to inevitable line broadening in the data processing. They coalesce with the central line increasing its integrated area. We refer to this coalesced line as the *observed peak.* Thus

$$\text{integral intensity of the observed peak} = N_W(1 - 0.1427N_{\text{corner}}) \quad (2)$$

For nuclei where N_{corner} is equal to or greater than 2, eq 2 must be modified[13] to take into account the population of molecules with two corner-sharing ^{183}W nuclei. The probability of having more than two ^{183}W neighbors is low and for practical purposes can be neglected.

The number of corner- and edge-sharings and the calculated relative intensities of the observed peaks in the ^{183}W NMR spectra of α-$[XW_{11}O_{39}]^{n-}$ (X = P, Si, B, etc.) are given in Table 2. These inferential results allow us to predict the actually observed relative integral intensities as 1.49:1.49:1.49:2.00:1.71:

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[12] *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987.

Table 3. ^{183}W NMR Chemical Shifts, $^{2}J_{W-O-P}$ Coupling Constants, and Integral Intensities for **1** and **3**[a]

	1			**3**			
atom	δ (ppm)	$^{2}J_{W-O-P}$ (Hz)	obsd integral intensity	δ (ppm)	$^{2}J_{W-O-P}$ (Hz)	obsd integral intensity	predicted integral intensity
$W_{1,2}$	−111.4	2.4	1.5	−1.3	2.2	1.5	1.49
$W_{3,4}$	−153.1	1.4	1.6	−158.6	0.6	1.5	1.49
$W_{5,8}$	−131.5	1.4	1.4	−128.0	0.3	1.4	1.49
$W_{6,7}$	−101.0	1.7	2.0	−43.7	1.6	2.0	2.00
W_{9}	−116.1	1.7	0.7	−126.4	2.5	0.7	0.75
$W_{10,11}$	−96.3	1.1	1.8	−109.7	0.9	1.6	1.71

[a] Aqueous solutions of the potassium salt of **1** (0.07 M) and the lithium salt of **3** (ca. 0.2 M).

0.75 (compare to the experimental results in Table 1) instead of 2:2:2:2:2:1 if all satellites could be observed and included in the integration. Despite the fact that ^{183}W NMR signals are narrow, we do not expect very accurate results from the integration. However, the difference is easily detectable and can be used for signal differentiation. Differences in the values of the chemical shifts should not affect this intensity ratio in the ^{183}W NMR spectrum of any diamagnetic α-$[XW_{11}O_{39}]^{n-}$.

Peak Heights. The observed tungsten resonances have both different integral intensities and heights. The peak height is related not only to the number of large (corner) coupling constants but also to the number of small (edge) coupling constants. A greater number of edge-sharing coupling constants broadens the base of the signal and decreases the peak height, while the integral intensity of the central peak with overlapping satellites remains the same. However *quantitative* predictions of this effect are practically impossible because the corresponding satellites are located asymmetrically around the central peak and the degree of overlap is hard to estimate. Nevertheless, tungstens with the same numbers of corner-shared but different numbers of edge-shared couplings can be distinguished on the basis of their relative peak heights. For example, in the spectra of α-$[XW_{11}O_{39}]^{n-}$, $W_{3,4}$, and $W_{5,8}$ (Figure 1) have the same integral intensities but different peak heights due to the different number of edge-shared couplings. The observed peak of $W_{5,8}$ is broader and shorter than that of $W_{3,4}$, which has only one edge-sharing constant (Table 2). The height of the $W_{5,8}$ signal is indeed smaller than that of $W_{3,4}$ in all reported spectra of diamagnetic undecatungstates.[3−5,10] In the absence of any other couplings, as in the case of α-$[SiW_{11}O_{39}]^{8-}$, the following pattern of peak heights should be observed: $W_{1,2} > W_{3,4} > W_{5,6}$ (Figure 1b). In undecatungstophosphates, however, the $^{2}J_{W-O-P}$ coupling constants should be also taken into consideration, as $^{2}J(W_{1,2},P)$ is relatively large and decreases the peak height of $W_{1,2}$ significantly.

We summarize our approach as follows:

1. *Satellites which do not overlap with the central peak decrease its integral intensity proportionally to the number of corresponding coupling constants.* This effect can be calculated[13] and measured by integration of the observed central signal. Counting of coupling constants includes all spin−spin interactions experienced by the nucleus, except that with the nucleus having the same chemical shift. For example, in the ^{183}W NMR spectra of α-$[XW_{11}O_{39}]^{n-}$, W_9 exhibits two couplings to $W_{10,11}$ which, in turn, experience only one coupling to W_9. The coupling between W_{10} and W_{11} is not observable.

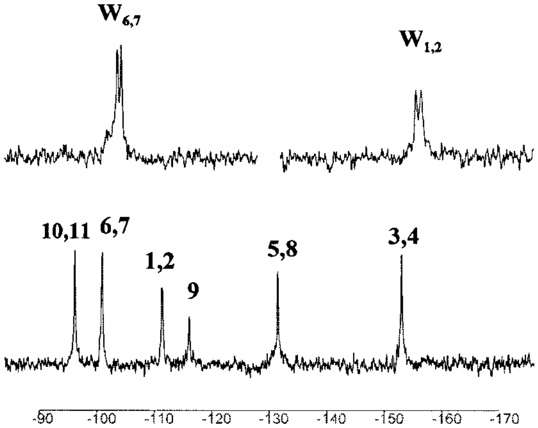

Figure 2. ^{183}W NMR spectrum of **1** and the expanded regions of signals $W_{1,2}$ and $W_{6,7}$.

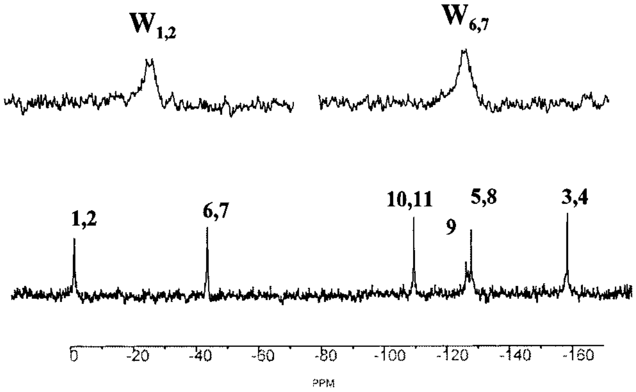

Figure 3. ^{183}W NMR spectrum of **3** and the expanded regions of signals $W_{1,2}$ and $W_{6,7}$.

2. *Couplings which overlap with the central peak do not affect its integral intensity but decrease its height. Two signals with the same integral intensities but different numbers of small coupling constants can be discriminated by the heights of their peaks.* Table 3 and Figures 2 and 3 illustrate the application of this method to spectra of a potassium salt of **1** and a lithium salt of **3** in which ^{183}W−^{183}W NMR couplings are not clearly observed. For integration purposes, the intensity of the largest peak was assigned a value of 2.00. Line broadening (LB values from 0.3 to 1.5 Hz) did not affect the relative integral intensities to any noticeable extent. Values of $^{2}J_{W-O-P}$ and integral intensities were measured at LB = 0.3 and 1.0 Hz, respectively.

Both spectra can be assigned on the basis of a combination of relative integrated intensities (Table 3) and relative peak heights ($W_{3,4} > W_{5,8} > W_{1,2}$ for reasons explained above). The resulting order of chemical shifts for the potassium salt of **1** is

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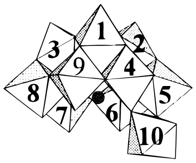
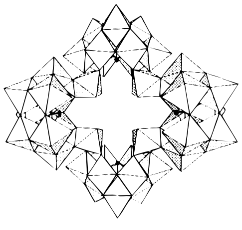
(13) The correction to eq 2 is small and can be evaluated as follows. Each pair of ^{183}W neighbors, about 2% of the ^{183}W nuclei under observation, will produce a doublet of doublets, if nonequivalent, or a triplet, if equivalent. In both cases, the central part of this signal, an additional $0.5(0.1427)^2$%, will overlap with the coalecsed peak. At the same time, the probability to find a tungsten without any ^{183}W corner-sharing neighbors is $(1 - 0.1427)^{N_{corner}}$. For these reasons, the corrected equation will be (for $N_{corner} \geq 2$)

$$\text{integral intensity} = N_W((0.8573)^{N_{corner}} + 0.0102(N_{corner}!)/(2!(N_{corner} - 2)!)) \quad (3)$$

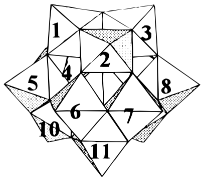
Table 4. Numbers of Corner- and Edge-Sharings and Calculated Intensities of the Coalesced Peaks in the ^{183}W NMR Spectrum of $[As_4W_{40}O_{140}]^{28-}$ Containing α-BAsW$_9$ Subunits

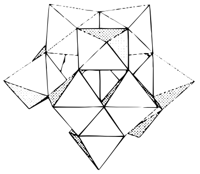




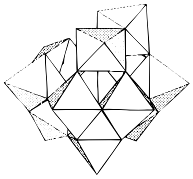
atom	corner-sharings	edge-sharings	integral intensity	relative no. of atoms
W_1	2	2	0.75	1
$W_{2,3}$	1	2	1.71	2
$W_{4,9}$	2	1	1.49	2
$W_{5,8}$	2	2	1.49	2
$W_{6,7}$	0	2	2.00	2
W_{10}	4	0	0.60	1

Table 5. Calculated Intensities of the Coalesced Peaks for β Isomers of Keggin Ions





β_1

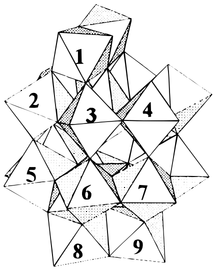


β_3

β_1, W_{10} removed	corner-sharings	edge-sharings	integral intensity	no. of atoms
W_1	2	2	0.75	1
$W_{2,3}$	2	1	1.49	2
$W_{4,5}$	2	1	1.49	2
$W_{6,9}$	2	2	1.49	2
$W_{7,8}$	1	2	1.71	2
$W_{11,12}$	0	2	2.00	2

β_3, W_1 removed	corner-sharings	edge-sharings	integral intensity	no. of atoms
$W_{2,3}$	2	0	1.74	2
$W_{4,5}$	1	2	2.00	2
$W_{6,9}$	2	2	1.74	2
$W_{7,8}$	1	2	2.00	2
W_{10}	2	2	0.87	1
$W_{11,12}$	1	2	2.00	2

Table 6. Numbers of Corner- and Edge-Sharings and Calculated Intensities of the Central Set of Lines in the ^{183}W NMR Spectrum of α_2-$[X_2W_{17}O_{61}]^{n-}$



atom	corner-sharings	edge-sharings	integral intensity	no. of atoms
W_1	2	0	1.74	2
W_2	3	0	1.54	2
W_3	3	1	1.54	2
W_4	1	1	2.00	2
W_5	3	0	1.54	2
W_6	3	1	1.54	2
W_7	2	1	1.74	2
W_8	2	1	1.74	2
W_9	2	2	0.87	1

identical to that of the (more soluble) sodium salt[5a] but is strikingly different from that of the lithium salt (Figure 1, Table 1).[14]

Three more examples, summarized in Tables 4−6, serve to illustrate the power and limitations of the method.

Thouvenot et al.[6] have assigned the spectra of the cryptate anion $[NH_4As_4W_{40}O_{140}]^{27-}$ using 1D-COSY techniques. As shown in Table 4, a complete assignment can also be made from the peak intensities and heights. Of the two signals with equal intensities, $W_{4,9}$ and $W_{5,8}$, the former is predicted to be the taller and is shown to be so in Figure 5 of ref 6.

Three lacunary derivatives of the β isomer of the Keggin anion are known. Two of these (β_1 and β_3) have C_s symmetry and will have six-line ^{183}W NMR spectra. The predicted intensity patterns of these isomers (Table 4) will be sufficiently distinct (2.0:1.8:1.5:1.5:1.5:0.8 vs 2.0:2.0:2.0:1.7:1.7:0.9) to permit easy identification.

The relative observed peak intensities for the lacunary anions α_2-$[X_2W_{17}O_{61}]^{10-}$ (X = P, As), Table 6, show that, for certain structures, only a partial assignment can be made from intensity/height observations. In this example, apart from recognition of W_4 and W_9, the peak height of W_1 should be greater than those of W_7 and W_8 and the lines for W_2 and W_5 should be taller than those for W_3 and W_6.[15]

Conclusions

We have shown that the intensity patterns in 1D multiline ^{183}W NMR spectra of polyoxotungstates provide information leading to the complete or partial assignment of chemical shifts. This method can be applied to rapidly accumulated spectra (e.g., of metastable compounds) or to spectra of relatively poorly soluble complexes in which satellites arising from ^{183}W−^{183}W spin-coupling cannot be reliably observed or measured. This approach cannot compete with more powerful methods, such as 2D-INADEQUATE, but it is especially useful in cases where neither two-dimensional NMR spectroscopy nor straightforward observation of coupling constants is possible. The method requires that relaxation times of the various tungsten nuclei be of approximately similar magnitudes. Anions containing paramagnetic or quadrupolar (e.g., ^{51}V and ^{93}Nb) centers that can greatly increase relaxation rates for neighboring ^{183}W nuclei are not suitable candidates.

The method can also be applied to NMR spectra of other poorly abundant nuclei such as ^{195}Pt, ^{119}Sn, and ^{29}Si.

Acknowledgment. We thank Drs. Michael Dickman and Knut Wasserman for assistance with graphics and the National Science Foundation for support through Grant No. CHE-9727417.

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[14] This effect has been attributed to the formation of a tighly bound lithium complex.

[15] Kozik, M. Ph.D. Dissertation, Georgetown University, 1981; *Diss. Abstr. Int.* **1989**, *B49*, 2639.