Polyoxotungstates

Vicinal Tungsten–Tungsten Coupling Constants in Polyoxotungstates: DFT Calculations Challenge an Empirical Rule

Alessandro Bagno and Marcella Bonchio*

Nuclear magnetic resonance spectroscopy of the ^{183}W nucleus ($I = 1/2$, 14 % natural abundance) is an essential tool for the characterization of tungsten polyoxometalates (POMs). It provides direct information on the electronic environment of each nonequivalent tungsten atom of these compounds, which display a formidable structural diversity and a constantly increasing range of applications.[1,2]

Spin–spin coupling is observed between vicinal tungsten nuclei separated by one oxygen atom ($^2J_{WW}$), and gives rise to satellites having 7 % intensity of the main peak.[3] The analysis of such coupling constants is a traditional mainstay of POM characterization, but has been so far based on a mere empirical approach. The rationale for this is rooted in the two basic structural arrangements that WO_6 octahedra display in the POM cage, that is, edge- or corner-sharing junctions. The two cases differ in W-O-W angle, which lies in typical ranges of 120–130° (edge-sharing) and 140–150° (corner-sharing).[1] There is much empirical evidence that the corresponding values of $^2J_{WW}$ take on values of 5–12 and 15–30 Hz, respectively, and this criterion is extensively applied in the assignment of POM spectra, based on the assumption that the W-O-W angle is the sole factor involved.[4] However, there has been no clear indication of

[*] Prof. A. Bagno
Department of Chemistry, University of Padova
via Marzolo 1, 35131 Padova (Italy)
Fax: (+39) 0498275239
E-mail: alessandro.bagno@unipd.it
Dr. M. Bonchio
CNR Institute for Membrane Technology
Padova Section, via Marzolo 1, 35131 Padova (Italy)

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whether other structural or electronic factors contribute to the observed $^2J_{WW}$ values, so the scope of this empirical criterion remains somewhat uncertain.

Instances are indeed known where this paradigm has led to ambiguous conclusions: a cogent and timely example is provided by POMs derived from the γ-$[XW_{10}O_{36}]^{n-}$ (X = P, Si) structure, which have promising applications in catalysis and materials science.[5] In aqueous solution, the tungstosilicate anion γ-$[SiW_{10}O_{36}]^{8-}$ exhibits a three-line (2:2:1) ^{183}W spectrum with three $^2J_{WW}$ couplings (Figure 1).[6] The NMR

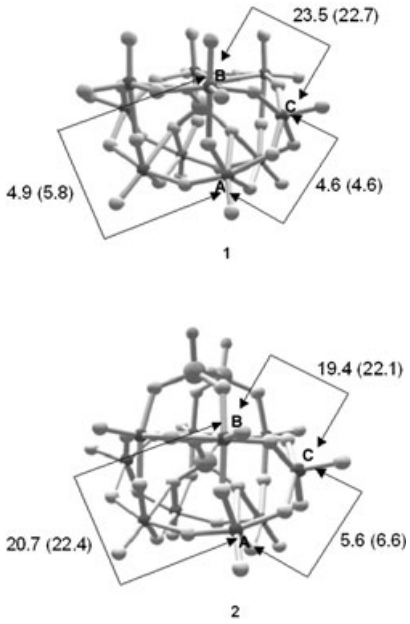


Figure 1. Structures of γ-$[SiW_{10}O_{36}]^{8-}$ (**1**) and γ-$[(HSi)_2OSiW_{10}O_{36}]^{4-}$ (**2**) with experimental and calculated (in parentheses) $^2J_{WW}$ couplings.

parameters were obtained for the Li salt of the nonsymmetric monoprotonated form, but fast exchange on the NMR timescale renders the spectrum still consistent with C_{2v} symmetry (see below).

However, the coupling constants of 23.5 (BC), 4.6 (AC), and 4.9 Hz (AB) contrast with the empirical rule expecting two large corner couplings (BC and AB) and one small edge coupling (AC).[6] Conversely, the hybrid derivatives γ-$[(RSi)_2OSiW_{10}O_{36}]^{4-}$ show the expected corner AB coupling (20.7 Hz for R = H).[7] This evidence speaks against the generally accepted empirical correlation linking the magnitude of $^2J_{WW}$ couplings simply to the W-O-W angle of the junctions, which are preserved along the series of these isostructural complexes. The small $^2J_{WW}$ in the divacant precursor, despite its corner-sharing arrangement, was tentatively ascribed to a concurrent decrease of the W_A-O-W_B angle and an elongation of the W–O bond involving lacunary tungsten atom W_B.[7]

Here we provide a consistent set of computed coupling constants both for model fragments and complete POM systems, and show that 1) the W-O-W angle is the sole important factor *only* when the W–O distance has typical values or remains constant within the series examined, and 2) the electronic structure of the surroundings farther than one bond away does not affect these couplings significantly. Finally, we confirm the proposed structure assignment of the two decatungstates, provide a rationale for the observed anomaly, and address structure equilibria in aqueous solution.

Further pursuing our aim of devise a reliable computational approach to predict ^{183}W NMR parameters,[8] we made use of the ADF DFT code[9] for relativistic calculations of NMR coupling constants[10] by means of the ZORA approximation.[11] Owing to the very high computational cost of such calculations on systems as large as those dealt with here, preliminary calculations were run on a model system consisting of two oxotungstate fragments $[O_4W\text{-}O\text{-}WO_4]^{6-}$ (Figure 2), which allowed the coupling surface to be scanned.[12,13]

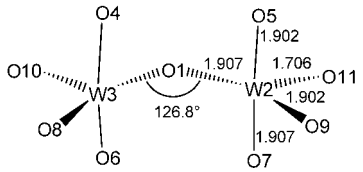


Figure 2. Internal coordinates of the $[O_4W\text{-}O\text{-}WO_4]^{6-}$ system. The W-O-W angle was set to 126.8° for edge-sharing (as in the figure) or 152.4° for corner-sharing, respectively. For the coupling surface scan, the O5-W2-O1-W3 dihedral angle was set to 85.3°. See Supporting Information for other geometrical parameters.

For initial testing, the W2-O1-W3 angle was set to 126.8° (edge) or 152.4° (corner), and the W2–O1 distance to 1.907 Å. Both fragments were optimized at the BP-ZORA scalar/TZ2P level, and coupling constants were calculated at the same level. We thus obtained values of 26.5 and 8.4 Hz for corner and edge couplings, respectively.[14] The corresponding values at the ZORA spin–orbit level (25.7 and 8.2 Hz, respectively) are very similar, as is commonly found.[11]

All further calculations were carried out at the BP-ZORA scalar/TZ2P level.[15] We then scanned the $[O_4W\text{-}O\text{-}WO_4]^{6-}$ coupling surface as a function of the W–O distance (r_{WO} = 1.80–2.20 Å) and the W-O-W angle (α = 120–160°), whereas the O5-W2-O1-W3 dihedral angle was kept constant at 85.3°.[16]

Figure 3 shows that a smooth decrease in $^2J_{WW}$ is predicted with decreasing α and increasing r_{WO}. The calculated angular dependence conforms with the accepted picture. Moreover, a marked dependence on distance is also revealed, especially at large α values.[17] Thus, for α = 150° the dependence on distance is sufficiently pronounced that such couplings encompass a fairly wide range (15–22 Hz) just by varying r_{WO} within reasonable bounds.

Hence, this model allows the magnitude of the sought coupling constants as a function of r_{WO} and α to be predicted. However, the coupling surface was determined for, among others, fixed O5-W2-O1-W3 dihedral angle and O1-W2-O5 angle; these are expected to differ among various tungsten sites, and the two W–O distances are normally not equal. Thus, actual couplings may depend on further geometrical variables. Moreover, electronic effects of other atoms are not

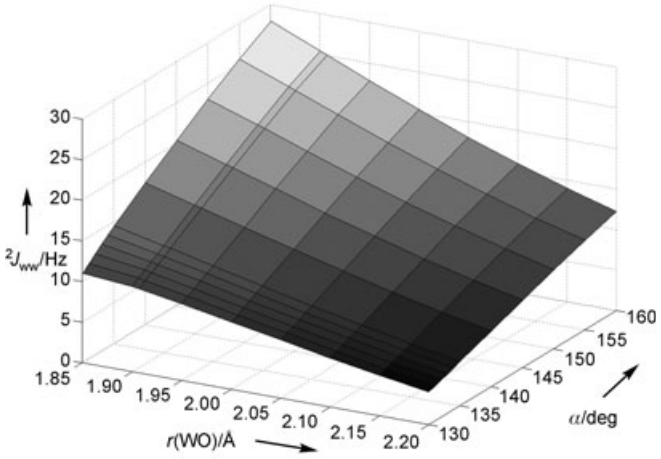
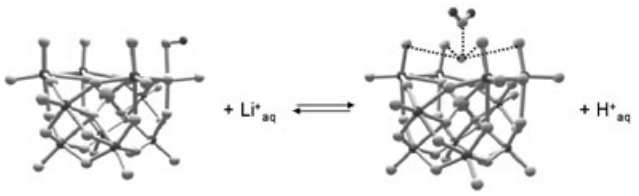


Figure 3. $^2J_{WW}$ coupling surface of the $[O_4W\text{-}O\text{-}WO_4]^{6-}$ system. Numerical data are collected as Supporting Information.

taken into account. However, a key point was provided by the recognition that reducing the basis set of the terminal (O4–O11) or the bridging (O1) oxygen atoms to frozen-core basis sets of DZ or TZ2P quality[18] only slightly affected the calculated coupling.[19] Hence, the typical range of couplings is preserved even when the coupled nuclei are computationally "severed" from the rest of the POM, which implies that its electronic structure is expected to have little if any effect. It is then possible to run a coupling calculation on a complete POM structure, provided that all atoms except the W-O-W triad being investigated are modeled at a relatively low level. In this way, one can include all structural factors in the calculation at a reasonable cost.

We have applied this concept to γ-$[SiW_{10}O_{36}]^{8-}$ and γ-$[(HSi)_2OSiW_{10}O_{36}]^{4-}$ (Figure 1). The speciation of the parent lacunary anion and the counterion effect (H^+ or Li^+) on the NMR parameters was also addressed by considering two limiting forms undergoing fast exchange[6]: monoprotonated γ-$[SiW_{10}O_{36}H]^{7-}$ and the inclusion complex γ-$[Li(H_2O)SiW_{10}O_{36}]^{7-}$ (Scheme 1). The solution structure of



Scheme 1. Proposed speciation[6] of γ-$[SiW_{10}O_{36}]^{8-}$ in aqueous solution, with equilibrium between the monoprotonated form γ-$[SiW_{10}O_{36}H]^{7-}$ (left) and the Li complex γ-$[Li(H_2O)SiW_{10}O_{36}]^{7-}$ (right).

these polyoxoanions is a matter of debate owing to the known influence of the counterion on their spectroscopic properties,[8] stability, and catalytic activity.[5]

After geometry optimization,[8] the relevant W and O atoms were treated at the usual TZ2P level, and all other atoms with small basis sets.[20] The results[21] for γ-$[SiW_{10}O_{36}]^{8-}$ and γ-$[(HSi)_2OSiW_{10}O_{36}]^{4-}$ match very well the experimental values (Figure 1): in the divacant POM, J_{AB} has a value typical of an edge coupling, even though the W-O-W angle (144°) is typical of a corner junction. By comparison with the coupling surface, this is understood as arising from a longer W–O distance in the divacant POM (2.06 Å) than in the hybrid derivative (1.94 Å).

Neither protonation nor inclusion of Li^+ causes a change in W-O-W angles. However, protonation brings about a marked shortening of the average W–O bond (2.06 to 1.96 Å); the other W–O distances are unchanged.[22] Consistent with the shorter distance, J_{AB} is larger (16.7 Hz). Under conditions of fast exchange among all four lacunary oxygen atoms (for which the previous value can still be assumed, since the local geometries are not affected), an average value of about 8.5 Hz can be estimated. Inclusion of $Li(H_2O)^+$ in the lacuna entails opposite effects: the average W–O distance is enlarged to 2.15 Å, and correspondingly J_{AB} decreases to 4.6 Hz. Assuming equal populations at equilibrium, one can estimate an average of 6 Hz, and the net result is very similar to that of the isolated divacant species.

In conclusion, empirical arguments based on the relationship between the magnitude of $^2J_{WW}$ and corner- versus edge-sharing octahedra must be looked upon carefully, since situations may arise in which the W–O distance is an important or even controlling factor. Even though these couplings appear to be a local property of each WOW triad, they may probe longer range interactions (protonation, counterions, etc.) insofar as these reflect changes in the main structural variables (r_{WO} and α).

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[1] *Polyoxometalates* (Ed.: C. L. Hill), thematic issue of *Chem. Rev.* **1998**, *98*, 1–390.
[2] *Polyoxometalate Chemistry for Nano-Composite Design* (Eds.: T.Yamase, M. Pope), Kluwer, Plenum, New York, **2002**, pp. 1–232.
[3] Y.-G. Chen, J. Gong, L.-Y. Qu, *Coord. Chem. Rev.* **2004**, *248*, 245–260.
[4] C. Brevard, R. Schimpf, G. Tourne, C. M. Tourne, *J. Am. Chem. Soc.* **1983**, *105*, 7059–7063.
[5] a) M. Bonchio, M. Carraro, G. Scorrano, A. Bagno, *Adv. Synth. Catal.* **2004**, *346*, 648–654; b) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964–966; c) C. R. Mayer, V. Cabuil, T. Lalot, R. Thouvenot, *Angew. Chem.* **1999**, *111*, 3878–3881; *Angew. Chem. Int. Ed.* **1999**, *38*, 3672–3675.
[6] J. Canny, A. Tézé, R. Thouvenot, G. Hervé, *Inorg. Chem.* **1986**, *25*, 2114–2119.
[7] C. R. Mayer, I. Fournier, R. Thouvenot, *Chem. Eur. J.* **2000**, *6*, 105–110. Coupling constants were reported for a similar derivative exhibiting very similar behavior to the POM discussed here.
[8] A. Bagno, M. Bonchio, A. Sartorel, G. Scorrano, *ChemPhysChem* **2003**, *4*, 517–519.

[9] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca-Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931–967.
[10] a) J. Autschbach, T. Ziegler, *J. Chem. Phys.* **2000**, *113*, 936–947; b) J. Autschbach, T. Ziegler, *J. Chem. Phys.* **2000**, *113*, 9410–9418.
[11] J. Autschbach, T. Ziegler in *Calculation of NMR and EPR Parameters* (Eds.: M. Kaupp, M. Bühl, V. G. Malkin), Wiley-VCH, Weinheim, **2004**.
[12] We employed the Becke88 exchange plus the Perdew86 correlation functional (BP) with basis sets composed of Slater functions optimized for ZORA calculations.[9] We used double-ζ or triple-ζ basis sets, the latter with a single or double set of polarization functions on all atoms (DZ, TZP, and TZ2P, respectively), with frozen core orbitals where appropriate. Relativistic core potentials were generated with the Dirac utility.
[13] This arrangement was obtained by cutting off the relevant fragments from the calculated structure of α-$[PW_{11}O_{39}]^{7-}$.[8]
[14] See the Supporting Information for details. DSO, PSO, FC, and SD denote the diamagnetic and paramagnetic spin–orbit, Fermi contact, and spin–dipole contributions. All couplings are dominated by the FC term, which accounts for 90–95% of the total.
[15] Only the DSO, PSO, and FC terms were calculated; the DSO term never exceeded 2 mHz.
[16] Although most POMs bear remarkably large negative charges (up to −12), solvent effects on coupling constants are hardly known, consistent with their low charge density (q/m ratio; see X. López, C. Bo, J. M. Poblet, *J. Am. Chem. Soc.* **2002**, *124*, 12574–12582 for a discussion of its implications). Thus, isolated-ion modeling is probably suitable, despite the higher q/m of the model system. Work is in progress to address this issue.
[17] At very small r_{WO} and α values large negative values are predicted (see Supporting Information). However, this region is probably incompatible with the cage structures of POMs.
[18] Both basis sets had the 1s shell frozen, that is, not participating in the SCF procedure. Owing to their insufficient flexibility in the critical region near the nucleus, these basis sets are not recommended for these calculations.[9]
[19] At $r_{WO} = 1.907$ Å, $\alpha = 160°$ the calculated coupling decreased from 25 Hz to 23 Hz.
[20] All basis sets of DZ quality. W: 4f shell frozen; O: 1s shell frozen; Si: 2p shell frozen. No core was frozen for H and Li.
[21] The relative contributions of FC and PSO terms (Supporting Information) follow the same trend as the model system.
[22] See the Supporting Information for details of bond lengths.

