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Effect of Positional Isomerism and Vanadium Substitution on ^{51}V Magic Angle Spinning NMR Spectra of Wells-Dawson Polyoxotungstates

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Abstract

We examined the effect of positional isomerism and vanadium substitution on the ^{51}V magic angle spinning NMR spectra of potassium salts of vanadium-substituted polyoxotungstates of the Wells-Dawson series. NMR parameters of this class of catalytically active polyoxotungstates are reported. Multiple species, indicative of differences in the local environment at the substitution sites, are observed in solid-state NMR spectra of the di- and tri-substituted complexes in contrast to solution NMR spectra, where single average chemical shift was observed. The quadrupolar and chemical shift anisotropy parameters depend strongly on the position and the degree of the vanadium substitution into the oxoanion core establishing ^{51}V SATRAS NMR spectroscopy as a sensitive probe of the local electronic environment in these catalytically active solids.

Graphical Abstract

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Keywords

solid-state NMR; magic angle spinning; ^{51}V ; polyoxometalate; POM; Wells-Dawson; polyoxoanion; oxotungstate; quadrupolar coupling; chemical shift anisotropy

1. Introduction

Wells-Dawson phosphotungstates are known since 1892, when the synthesis of the first compound of the series was reported by Kehrman [1]. The first crystal structure was reported by Dawson in 1953. Since the first discovery of the Wells-Dawson anion, these compounds have found a wealth of applications due to their versatile chemical and physical properties [2]. Wells-Dawson heteropolyoxometalates are utilized as heterogeneous and homogeneous catalysts in various types of processes, in solution and gas phase [2]. Vanadium-substituted polyoxoanionic compounds are used as catalysts in oxidation of NADH, aerobic oxidation of alkyl aromatic compounds, selective epoxidation of alkenes and alkenols with H_2O_2 , benzene hydroxylation with H_2O_2 , toluene and nitrobenzene oxidation with H_2O_2 (reviewed by Briand et al. [2]).

Vanadium derivatives of Wells-Dawson polyoxoanions are efficient in catalyzing the vapor-phase dehydrogenation of cyclohexanol [3], oxidation of tetralin by molecular oxygen [4], direct conversion of light C_1 - C_3 alkanes into the corresponding carboxylic acids [5], and other transformations [6–10]. In all of the above cases vanadium substitution enhances dramatically the catalytic activity of the oxoanions, suggesting that vanadium modulates the electronic structure of the anion affecting the redox potentials. Vanadium-substituted polyoxometalates with enhanced activities for heterogeneous catalysis of hydrocarbon oxidation are generated as supported on mesoporous MCM-41 [11]. Due to these expanding applications of Wells-Dawson heteropolycompounds in catalysis, the interest toward development of novel representatives of this family continues to grow [12–15].

To gain insight on the structure-function relationships of the Wells-Dawson heteropolycompounds, understanding the mechanism by which vanadium fine-tunes the chemical reactivity of the catalyst is necessary. This understanding includes the knowledge of both the three-dimensional geometry of the extended solid (available from the single crystal X-ray diffraction in the cases where the solid can be crystallized) and the electronic structure of the anion and of vanadium center in particular. Advancements in theoretical quantum chemical methods have allowed for the investigations of Wells-Dawson (and generally polyoxometalate solids) [16–20], and these studies are expected to aid in the interpretation of the experimental structural and spectroscopic data. We and others have shown that ^{51}V solid-state NMR spectroscopy can be used as a sensitive reporter of the structural and electronic environment of vanadium sites in a wide variety of inorganic and bioinorganic solids [21–39] including polyoxometalates [40–42]. Specifically, in our previous MAS NMR studies on Lindqvist and Keggin polyoxotungstate solids, we have demonstrated that insights unavailable from X-ray diffraction and other structural methods could be gained, namely that counter cations and the degree of vanadium substitution modulate the electronic structure of the oxoanion as is evident in the ^{51}V magic angle

spinning (MAS) NMR spectra [40, 41] as well as vibrational spectra [16]. Since Wells-Dawson polyoxometalates have been utilized for homogeneous and heterogeneous catalysis, characterization of the electronic and structural properties of these complexes in both liquid and solid phase is needed to investigate their catalytic activities, dependence on metal ion substitution, and redox properties. This work establishes ^{51}V MAS NMR spectroscopy as a quick non-destructive structural probe in polyoxometalate solids that is especially useful in the absence of long-range order and for the investigation of electronic properties of these complexes as catalysts in solid phase.

In this study, we assess the utility of ^{51}V MAS NMR spectroscopy for structural analysis of vanadium-substituted heteropoly compounds of Wells-Dawson family. We present an investigation of four vanadium-substituted Wells-Dawson solids. In contrast to solution NMR spectroscopy, multiplet patterns were observed for di- and tri-substituted complexes, indicating that the different vanadium atoms are magnetically non-equivalent in the solid state. The results reveal that the ^{51}V NMR parameters in these polyoxotungstates depend on the degree and the position of vanadium substitution into the oxoanion thus indicating that ^{51}V MAS NMR spectroscopy is a sensitive probe of local environment of vanadium in the Wells-Dawson type of compounds.

2. Materials and Methods

2.1. Materials and Syntheses

All chemicals were obtained from Aldrich or Fisher and used without further purification: sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) and sodium metavanadate (NaVO_3) were purchased from Aldrich Chemicals. Hydrochloric acid, phosphoric acid (85%), sulfuric acid, and bromine were purchased from Fisher Scientific.

1-K₇P₂VW₁₇O₆₂•18H₂O (α_2 -isomer) (I) was obtained with 10 g yield (40.6%) from 25 g α_2 -K₇P₂W₁₇O₆₁•20H₂O according to the published procedure [43].

4-K₇P₂VW₁₇O₆₂•17H₂O (α_1 -isomer) (II) was obtained with 8 g yield (30%) from 25 g α_1 -K₇LiP₂W₁₇O₆₁•20H₂O according to the published procedure [43].

1,2 - K₈P₂V₂W₁₆O₆₂ (III) was obtained with 4.6 g yield (10%) from 25 g α_2 -K₇P₂W₁₇O₆₁•20H₂O according to the published procedure [43].

1,2,3 - K₉P₂V₃W₁₅O₆₂ (IV) was obtained with 2.8 g yield (15%) from 25 g α_2 -K₇P₂W₁₇O₆₁•20H₂O according to the published procedure [43].

The schematic representations of the structures of the corresponding oxoanions are depicted in Fig. 1.

2.2. Solution NMR Spectroscopy

^{51}V and ^{31}P solution NMR spectra were acquired at 9.4 T on a JEOL GSX-400 spectrometer equipped with Delta data system. The ^{51}V and ^{31}P resonance frequencies were 105.12 and 161.87 MHz, respectively. All spectra were acquired using a 5 mm broadband probe. ^{51}V spectra were acquired using a 5.8 μs (30°) single pulse; ^{31}P spectra were acquired with a 15 μs (90°) single pulse. 2048 complex FID points were collected. For ^{51}V , the total acquisition

time of 48.7 ms, and the recycle delay of 500 ms were used. For ^{31}P , a recycle delay of 2 s was used. The ^{51}V and ^{31}P spectra were processed with 2 Hz exponential line broadening; no zero filling was applied. The isotropic chemical shifts are reported relative to the neat VOCl_3 sample and H_3PO_4 (85%), respectively, used as the external reference.

2.3. Solid-State NMR Spectroscopy

Solid-state ^{51}V NMR spectra were acquired on a Tecmag Discovery spectrometer operating at 105.2 MHz (9.4 T). A 4 mm Doty XC4 MAS probe was employed. In general, 8–16 mg of samples were loaded into 4 mm Si_3N_4 rotors. For each compound, ^{51}V MAS NMR spectra were acquired at several spinning frequencies ranging from 4 to 17 kHz. The spinning frequencies were controlled to within ± 5 Hz. The vanadium chemical shifts were referenced with respect to neat VOCl_3 . The 90° pulse-widths of $3.1 \mu\text{s}$ ($\gamma B_1/2\pi \approx 80$ kHz) were employed (calibrated using neat liquid VOCl_3). The magic angle was set by maximizing the number of rotational echoes observed in the ^{23}Na NMR free-induction decay of solid NaNO_3 . All MAS spectra were acquired using a single-pulse excitation. 1 μs pulse was employed to excite the central and the satellite transitions. 1 s recycle delay was used. The spectral width was 1.25 MHz. A total of 4096 complex data points were acquired. The data were processed by linear prediction of the first points to suppress the baseline distortions, followed by Fourier transformation and baseline correction.

2.4. Simulations of the NMR Spectra

Numerical simulations of the experimental ^{51}V solid-state NMR spectra were performed on a 1.1 GHz Pentium-4 PC under Linux environment using SIMPSON [44]. The combined effects of the quadrupolar interaction to second order and chemical shielding anisotropy were taken into account in the simulations. The seven independent parameters describing the quadrupolar and CSA tensor anisotropies (C_Q , η_Q , δ_σ and η_σ) and the relative tensor orientations (the Euler angles α , β and γ) were obtained by the least-squares fitting of the simulated and experimental sideband intensities using a home-written program in Mathematica 4.0 (Wolfram, Inc.). The effect from the non-uniform detection (i.e. the quality factor (Q) of the probe circuitry) has been taken into account in the simulations. The quadrupolar coupling parameters (C_Q and η_Q) and the anisotropic chemical shielding parameters (δ_σ and η_σ) are defined as described below. The Euler angles are defined as $0 < \alpha < \pi$, $0 < \beta < \pi/2$, and $0 < \gamma < \pi/2$.

The quadrupolar interaction parameters are defined as:

$$C_Q = \frac{eQV_{zz}}{h}; \quad \eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}}; \quad (1)$$

where C_Q is the quadrupolar coupling constant (in MHz); V_{xx} , V_{yy} , V_{zz} are the principal components of the electric field gradient (EFG) tensor, with $V_{zz} = eq$ being its largest principal component, and $|V_{zz}|$, $|V_{yy}|$, $|V_{xx}|$. C_Q defines the overall breadth of the spectral envelope. Q is the vanadium quadrupole moment ($-0.048 \times 10^{-28} \text{ V/m}^2$) [45]; e is the electronic charge; h is the Planck constant.

In this work, the standard notation is used for defining the components of the chemical shift anisotropy tensor [46]:

$$\delta_{\sigma} = \delta_{zz} - \delta_{\text{iso}}; \quad \eta_{\sigma} = \frac{\delta_{yy} - \delta_{xx}}{\delta_{zz} - \delta_{\text{iso}}}; \quad \delta_{\text{iso}} = \frac{1}{3} (\delta_{xx} + \delta_{yy} + \delta_{zz}) \quad (2)$$

δ_{iso} is the isotropic chemical shift, δ_{xx} , δ_{yy} , and δ_{zz} are the principal components of the CSA tensor. δ_{σ} is the reduced anisotropy of the CSA tensor determining the breadth of the tensor (throughout the text, we will refer to δ_{σ} as anisotropy). Note that according to Haeberlen-Mehring-Spiess, anisotropy of the CSA tensor is defined as $\delta = \delta_{zz} - (\delta_{xx} + \delta_{yy})/2$. We also note that the chemical shift anisotropy tensor is related to the chemical shielding anisotropy tensor as follows [47]:

$$\hat{\delta} = \hat{1}\sigma_{\text{iso}} - \hat{\sigma} \quad (3)$$

where $\hat{\delta}$ is the chemical shift tensor, $\hat{\sigma}$ is the chemical shielding tensor, $\hat{1}$ is the unit matrix, and σ_{iso} is the isotropic value of the chemical shielding of the reference compound, VOCl_3 . η_{σ} is the asymmetry parameter of the CSA tensor.

3. Results and Discussion

3.1. Characterization of Vanadium-Substituted Wells-Dawson Polyoxometalate Solids

Mono-vanadium (**I**, **II**), di-vanadium (**III**), and tri-vanadium (**IV**) substituted Wells-Dawson polyoxotungstates were prepared with potassium ions as the counteranion, as described in the experimental section. Multinuclear (^{51}V , ^{31}P) solution NMR spectra were acquired to confirm the structures. The ^{51}V and ^{31}P chemical shifts reported in Table 1 are in good agreement with the prior report [43]. The ^{51}V NMR spectra display a single resonance for di-, or tri-vanadium-substituted Wells-Dawson-type polyoxotungstate, representing symmetrical vanadium atoms in these species. The solution ^{31}P NMR spectra show two isotropic resonances, corresponding to the nonequivalent phosphorus sites due to the vanadium substitutions, as expected.

3.2. ^{51}V MAS NMR Spectra of Vanadium-Substituted Wells-Dawson Solids

The ^{51}V MAS NMR spectra of **I** - **IV** acquired at a spinning frequency of 10 kHz are presented in Fig. 2. The isotropic chemical shifts are marked with asterisks. The insets represent the expansions of the spinning side bands around the low and high frequency side of the highest intensity resonance. The ^{51}V NMR spectra of the central and satellite transitions display a single set of spinning side bands from their di-, or tri-vanadium substitution (see Fig. 2 (c) and (d)), as expected from the symmetry of the anion. As shown in Fig. 1, the mono-vanadium substituted Wells-Dawson polyoxotungstates have two isomers: (1) α_2 isomer (**I**) with the vanadium atom in the cap; and (2) α_1 isomer (**II**) with the vanadium atom in the belt. Interestingly, the ^{51}V NMR spectra of **I** and **II** shown in Fig. 2 (a) and (b) exhibit significant differences in their spectral envelopes and lineshapes, consistent with the distinct local environments of vanadium atoms in these two species. A

much broader envelope was observed in **II** (α_1 isomer), as compared with **I** (α_2 isomer), reflecting a more distorted charge distribution around vanadium atom in this species. The spectral envelope width in the cap-substituted **I**, **III** and **IV** increases with degree of vanadium substitution (mono- < di- < tri-).

The experimental and simulated NMR spectra of **I** – **IV** at three spinning frequencies are presented in Fig. 3. The simulated best-fit spectra are in good agreement with experiment (RMSD values below 11%). The best-fit parameters are given in Table 2. The substitution on the belt (**II**) yields a quadrupolar-coupling constant of 1.73 MHz, which is the largest among the Wells-Dawson-type derivatives we have studied so far. This large quadrupolar coupling constant indicates that the vanadium environment in this compound is the most asymmetric. Additionally, the counter cation environment in this solid may be different from the compounds substituted in the cap. As we have reported previously for the ^{51}V NMR studies in Lindqvist and Keggin solids, both countercations and vanadium substitution modulates the electric field gradient of the vanadium center giving rise to substantial variations in the quadrupolar coupling parameters [40, 41]. The current and prior results make it clear that counter cations have to be explicitly included in computational models, which to the best of our knowledge has only been done in one study - our prior work on computing the vibrational frequencies in Lindqvist solids [16]. It will be interesting in the future to conduct these studies on Wells-Dawson series of compounds as well.

3.3. Isotropic Chemical Shifts and Linewidths

The isotropic chemical shifts of **I**–**IV** are shown in Table 1. The isotropic chemical shifts in solids were corrected for the second-order quadrupolar-induced shifts (equation 4 below) [48]. For the Wells-Dawson complexes with cap substitution, the ^{51}V isotropic chemical shifts in solution and solids differ only slightly by 0.1 to 3.3 ppm. The belt-substituted compound exhibits a larger difference (by 10 ppm). Such a large difference in solution and solid isotropic chemical shifts may arise from thermal and solvent effects in solution [49], suggesting that the vanadium center in belt-substituted compounds may experience larger solvation effects than compared to cap substitution. It is noteworthy that the belt-substituted complex in this series also exhibits the largest quadrupolar coupling (Table 2). In both the solution and solid state, the isotropic chemical shifts are sensitive to the degree of vanadium substitution. In the tri-vanadium-substituted **IV**, the vanadium atoms are more deshielded, with isotropic chemical shift of -500.6 ppm. In contrast, in the mono- and di-substituted compounds, the vanadium atoms are more shielded as suggested by the isotropic chemical shifts of these complexes (Table 1).

$$\delta_{\text{observed}} - \delta_{\text{iso}} = \frac{-3 \times 10^6 (e^2 q Q / h)^2 [I(I+1) - 9m(m-1) - 3] \left[1 + \frac{\eta^2}{3} \right]}{40 (v_0^2) [I(2I-1)]^2} \quad (4)$$

where $(e^2 q Q / h)$ is the quadrupolar coupling constant (C_Q , in MHz), I is the spin number; $I=7/2$ for ^{51}V ; m is the magnetic spin number ($m=1/2$ for the central transition), η is the

asymmetry of the quadrupolar tensor, ν_0 is the resonance frequency of the ^{51}V nucleus (105.2 MHz at 9.4T).

The insets in Fig. 2 display the lineshapes for the three individual spinning sidebands around the highest-intensity resonance in **I–IV**. The linewidths range from 17.4 to 36.3 ppm. For mono-substituted **I** and **II**, the NMR spectra exhibit the same line width of 17.4 ppm. The di- and tri-vanadium derivatives (**III** and **IV**) have broader linewidths of 20.3 and 36.3 ppm, respectively. As detailed in our previous work on Keggin complexes [41], homonuclear ^{51}V - ^{51}V dipolar coupling is expected to have a weak effect on linewidths of Wells-Dawson solids. In this context, it is worth noting that the Wells-Dawson structure possesses two identical “half units” of XM_9O_{31} , three-vacant lacunary α -Keggin structure, linked through oxygen atoms [2]. Therefore, the main contributions to the spectral linewidths in the Wells-Dawson solids arise from positional disorder with respect to the vanadium atoms and bulk morphology of the samples, similar to our prior observations in the Keggin solids.[41] Similar to the Keggin solids, the multiplet structures of individual spinning side bands suggest magnetically inequivalent vanadium sites in the crystal lattice of **II**, **III** and **IV**, rather than statistical distribution of vanadium orientations in the crystal lattice.

4. Conclusions

We presented a MAS NMR study of catalytically active mono-, di-, and tri- vanadium substituted oxotungstate solids. The parameters describing the magnitudes and relative orientation of the quadrupolar and chemical shift anisotropy tensors for a ^{51}V nucleus were determined from the manifold of spinning sidebands observed in the MAS spectrum for the central and satellite transitions. These ^{51}V NMR parameters in turn reflect the local electronic environment of ^{51}V nuclei for these compounds. Furthermore, multiplet patterns indicate that in di- and tri-substituted complexes vanadium atoms are magnetically non-equivalent, in contrast to when the complexes are in solution. The experimental NMR results indicate that the degree of substitution and the position of the vanadium substitution (cap vs. belt) influence the local electronic environment of the vanadium atoms. Therefore, this work demonstrates that the ^{51}V solid-state NMR can provide useful insights into the local structure of the vanadium sites in the vanadium-substituted polyoxotungstates of the Wells-Dawson family. Such studies will help in the understanding of the influence of vanadium substitution on the catalytic properties of polyoxometalates, particularly in solid phase.

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References

1. Kehrman F. Z. Anorg. Chem. 1892; 1:423–441.
2. Briand LE, Baronetti GT, Thomas HJ. Appl. Cat. A. 2003; 256:37–50.

3. Park DR, Kim H, Jung JC, Lee SH, Lee J, Song IK. *React. Kinet. Catal. Lett.* 2008; 93:43–49.
4. Razi R, Abedini M, Kharat AN, Amini MM. *Catal. Commun.* 2008; 9:245–249.
5. Kirillova MV, da Silva JAL, da Silva J, Pombeiro AJL. *Appl. Cat. A.* 2007; 332:159–165.
6. Maradur SP, Gokavi GS. *Catal. Commun.* 2007; 8:279–284.
7. Jing SB, Wang ZL, Zhu WC, Guan JQ, Wang GJ. *React. Kinet. Catal. Lett.* 2006; 89:55–61.
8. Keita B, Contant R, Mialane P, Secheresse F, De Oliveira P, Nadjo L. *Electrochem. Commun.* 2006; 8:767–772.
9. Sanchez LM, Sathicq ÁG, Baronetti GT, Thomas HJ, Romanelli GP. *Catal. Lett.* 2014; 144:172–180.
10. Ueda T, Ohnishi M, Shiro M, Nambu J-i, Yonemura T, Boas JF, Bond AM. *Inorg. Chem.* 2014; 53:4891–4898. [PubMed: 24784547]
11. Tangestaninejad S, Mirkhani V, Moghadam M, Mohammadpoor-Baltork I, Shams E, Salavati H. *Ultrason. Sonochem.* 2008; 15:438–447. [PubMed: 17692553]
12. Dong BX, Peng J, Chen YH, Zhang PP, Tian A, Chen J. *J. Mol. Struct.* 2008; 875:75–79.
13. Wang JP, Li SZ, Shen Y, Niu JY. *Cryst. Growth Des.* 2008; 8:372–374.
14. Sha JQ, Wang C, Peng J, Chen J, Tian AX, Zhang PP. *Inorg. Chem. Commun.* 2007; 10:1321–1324.
15. Tian AX, Han ZG, Peng J, Sha JQ, Zhai JL, Zhang PP, Chen J, Liu HS. *Z. Anorg. Allg. Chem.* 2007; 633:2730–2737.
16. Dmitrenko O, Huang WL, Polenova TE, Francesconi LC, Wingrave JA, Teplyakov AV. *J. Chem. Phys. B.* 2003; 107:7747–7752.
17. Lopez X, Bo C, Poblet JM. *J. Am. Chem. Soc.* 2002; 124:12574–12582. [PubMed: 12381202]
18. Wang JY, Hu CW, Jian M, Zhang J, Li GY. *J. Catal.* 2006; 240:23–30.
19. Watras MJ, Teplyakov AV. *J. Chem. Phys. B.* 2005; 109:8928–8934.
20. Liu C-G, Guan W, Song P, Su Z-M, Yao C, Wang E-B. *Inorg. Chem.* 2009; 48:8115–8119. [PubMed: 19639969]
21. Nielsen UG, Jakobsen HJ, Skibsted J. *Inorg. Chem.* 2000; 39:2135–2145. [PubMed: 12526525]
22. Pooransingh N, Pomerantseva E, Ebel M, Jantzen S, Rehder D, Polenova T. *Inorg. Chem.* 2003; 42:1256–1266. [PubMed: 12588164]
23. Ooms KJ, Bolte SE, Smee JJ, Baruah B, Crans DC, Polenova T. *Inorg. Chem.* 2007; 46:9285–9293. [PubMed: 17902653]
24. Polenova, T., Pooransingh-Margolis, N., Rehder, D., Renirie, R., Wever, R. V-51 Solid-State NMR Spectroscopy of Vanadium Haloperoxidases and Bioinorganic Haloperoxidase Mimics. Kustin, K.Pessoa, J.C., Crans, D.C., editors. *Vanadium: The Versatile Metal*; 2007. p. 178-202.
25. Ooms K, Polenova T, Shough AM, Doren DJ, Nash MJ, Lobo RF. *J. Phys. Chem. C.* 2009; 113:10477–10484.
26. Ooms KJ, Bolte SE, Baruah B, Choudhary MA, Crans DC, Polenova T. *Dalton Trans.* 2009:3262–3269. [PubMed: 19421628]
27. Smee JJ, Epps JA, Ooms K, Bolte SE, Polenova T, Baruah B, Yang LQ, Ding WJ, Li M, Willsky GR, la Cour A, Anderson OP, Crans DC. *J. Inorg. Biochem.* 2009; 103:575–584. [PubMed: 19201030]
28. Chatterjee PB, Goncharov-Zapata O, Quinn LL, Hou GJ, Hamaed H, Schurko RW, Polenova T, Crans DC. *Inorg. Chem.* 2011; 50:9794–9803. [PubMed: 21842875]
29. Goncharova-Zapata O, Chatterjee PB, Hou GJ, Quinn LL, Li MY, Yehl J, Crans DC, Polenova T. *CrystEngComm.* 2013; 15:8776–8783.
30. Gupta R, Hou GJ, Renirie R, Wever R, Polenova T. *J. Am. Chem. Soc.* 2015; 137:5618–5628. [PubMed: 25856001]
31. Li MY, Yehl J, Hou GJ, Chatterjee PB, Goldbourt A, Crans DC, Polenova T. *Inorg. Chem.* 2015; 54:1363–1374. [PubMed: 25590382]
32. Pourpoint F, Yehl J, Li M, Gupta R, Trebosc J, Lafon O, Amoureux JP, Polenova T. *Chemphyschem : a European journal of chemical physics and physical chemistry.* 2015; 16:1619–1626. [PubMed: 25825323]

33. Nielsen UG, Jakobsen HJ, Skibsted J. J. Chem. Phys. B. 2001; 105:420–429.
34. Nielsen UG, Boisen A, Brorson M, Jacobsen CJH, Jakobsen HJ, Skibsted J. Inorg. Chem. 2002; 41:6432–6439. [PubMed: 12444788]
35. Nielsen UG, Topsoe NY, Brorson M, Skibsted J, Jakobsen HJ. J. Am. Chem. Soc. 2004; 126:4926–4933. [PubMed: 15080698]
36. Nielsen UG, Hazell A, Skibsted J, Jakobsen HJ, McKenzie CJ. CrystEngComm. 2010; 12:2826–2834.
37. Eckert H, Wachs IE. J. Phys. Chem. 1989; 93:6796–6805.
38. Lapina OB, Khabibulin DF, Shubin AA, Tersikh VV. Prog. NMR Spec. 2008; 53:128–191.
39. Lapina OB, Mastikhin VM, Shubin AA, Krasilnikov VN, Zamaraev KI. Prog. NMR Spec. 1992; 24:457–525.
40. Huang W, Todaro L, Francesconi LC, Polenova T. J. Am. Chem. Soc. 2003; 125:5928–5938. [PubMed: 12733933]
41. Huang WL, Todaro L, Yap GPA, Beer R, Francesconi LC, Polenova T. J. Am. Chem. Soc. 2004; 126:11564–11573. [PubMed: 15366903]
42. Parker WO, Cavani F. J. Phys. Chem. C. 2015; 119:24003–24015.
43. Abbessi M, Contant R, Thouvenot R, Herve G. Inorg. Chem. 1991; 30:1695–1702.
44. Bak M, Rasmussen JT, Nielsen NC. J. Magn. Reson. 2000; 147:296–330. [PubMed: 11097821]
45. Hansen MR, Madsen GKH, Jakobsen HJ, Skibsted J. J. Chem. Phys. B. 2006; 110:5975–5983.
46. Schmidt-Rohr, K., Spiess, HW. Multidimensional Solid-State NMR and Polymers. London, San Diego, New York, Boston, Sydney, Tokyo: Hartcourt Brace & Company; 1999.
47. Facelli JC. Conc. Magn. Res. A. 2004; 20:42–69.
48. Kundla E, Samoson A, Lipmaa E. Chem. Phys. Lett. 1981; 83:229–232.
49. Gupta R, Yehl J, Li M, Polenova T. Can. J. Chem. 2015; 93:929–937.
50. Huang W, Vega AJ, Gullion T, Polenova T. J. Am. Chem. Soc. 2007; 129:13027–13034. [PubMed: 17918932]

Highlights

- ^{51}V MAS SATRAS spectroscopy is presented for analysis of vanadium-substituted Wells-Dawson polyoxotungstates
- ^{51}V quadrupolar and CSA parameters are sensitive reporters of position and degree of vanadium substitution into the oxoanion core

Figure 1.

The schematic representations of vanadium substituted polyoxotungstate anions: (a) 1-K₇P₂VW₁₇O₆₂•18H₂O (α₂-isomer) (I); (b) 4-K₇P₂VW₁₇O₆₂•17H₂O (α₁-isomer) (II); (c) 1,2 - K₈P₂V₂W₁₆O₆₂ (III); (d) 1,2,3 - K₉P₂V₃W₁₅O₆₂ (IV). The molecules are depicted in a ball-and-stick representation. In the anion, the tungsten atoms are shown in blue, the central P atoms are shown in orange, and the oxygen atoms are shown in red. The vanadium atoms are shown in green.

Figure 2.

Experimental ^{51}V MAS NMR spectra of (a) **I**, (b) **II**, (c) **III** and, (d) **IV** at 10 kHz. The isotropic chemical shift is indicated with an asterisk. The isotropic chemical shifts are compiled in Table 1 referenced with respect to neat VOCl_3 , used as an external referencing standard. The insets represent expansions of the spinning side bands around the low and high frequency side of the highest intensity resonance.

Figure 3.

Experimental ^{51}V NMR spectra acquired at MAS frequency of 8 kHz (blue), 10 kHz (black) and 13 kHz (brown) for (a) **I**, (b) **II**, (c) **III**, and (d) ^{51}V NMR spectra of **IV** at MAS frequency 10 kHz (blue), 13 kHz (black) and 15 kHz (brown). The gray traces below each experimental spectrum are the corresponding numerical simulations using the best-fit parameters as given in Table 2. The rmsd values between the experimental and the best-fit simulated spectra are shown next to each trace.

^{51}V and ^{31}P Isotropic NMR Chemical Shifts for the Vanadium-Substituted Wells-Dawson Polyoxotungstates (I–IV).

Table 1

Compounds	^{51}V Isotropic Chemical Shift in Solution, ppm (Experiment/Literature)	^{51}V Isotropic Chemical Shift in Solid State, ppm	Quadrupole Induced Shift, ppm	^{31}P Isotropic Chemical Shift in Solution, ppm	
				$\delta(\text{P1})^a$ (Experiment/Literature)	$\delta(\text{P2})^a$ (Experiment/Literature)
I 1-K ₇ P ₂ VW ₁₇ O ₆₂	–551.4/–553.8	–549.9	–0.2	–11.04/–10.84	–13.11/–12.92
II 4-K ₇ P ₂ VW ₁₇ O ₆₂	–572.3/–570.0	–558.6	–0.7	–11.64/–11.83	–12.72/–12.90
III 1,2-K ₈ P ₂ V ₂ W ₁₆ O ₆₂	–527.0/–527.5	–523.8	–0.4	–8.91/–8.82	–13.23/–13.44
IV 1,2,3-K ₉ P ₂ V ₃ W ₁₅ O ₆₂	–503.2/–501.3	–500.6, 486.1, 514.9 ^b	–0.6	–6.41/–6.25	–13.60/–13.90

^a: P1 is designated as the deshielded phosphorus atom which is closer to the vanadium atom in the Wells-Dawson oxotungstate anion while the shielded atom is designated as P2, following the previous nomenclature.[43]

^b: Isotropic chemical shift of the individual species as observed from the multiplet pattern for IV.

Table 2

Simulated ^{51}V Solid-State NMR Parameters for the Vanadium-Substituted Wells-Dawson Polyoxotungstates (**I–IV**).

	Compounds	C_Q (MHz)	Q_{eff}	δ_{iso} (ppm)	$ \Delta\sigma $ (ppm)	α (deg)	β (deg)	γ (deg)
I	1- $\text{K}_7\text{P}_2\text{VW}_{17}\text{O}_{62}$	0.88 ± 0.08	0.75 ± 0.23	454 ± 36	0.06 ± 0.04	33 ± 44	68 ± 4	31 ± 21
II	4- $\text{K}_7\text{P}_2\text{VW}_{17}\text{O}_{62}$	1.73 ± 0.01	0.37 ± 0.04	522 ± 16	0 $\pm$ 0	0–180	60 ± 0	63 ± 4
III	1,2- $\text{K}_8\text{P}_2\text{V}_2\text{W}_{16}\text{O}_{62}$	1.20 ± 0.07	0.80 ± 0.20	444 ± 21	0.03 ± 0.04	0 $\pm$ 0	45 ± 7	43 ± 5
IV	1,2,3- $\text{K}_9\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}$	1.57 ± 0.12	0.63 ± 0.42	373 ± 21	0.05 ± 0.03	0 $\pm$ 0	68 ± 29	44 ± 10