

Application of Solid State NMR to the Study of Heteropolyanions : Keggin Ions $[\text{SiW}_{12-x}\text{M}_x\text{O}_{40}]$, $\text{M} = \text{V}$ or Nb , $x = 1$ and 3

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Abstract: The mixed Keggin polyoxometalate salts $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, $K_8[\alpha\text{-SiW}_{11}\text{O}_{39}]$, $K_5[\alpha\text{-SiW}_{11}\text{VO}_{40}]\cdot x\text{H}_2\text{O}$, $K_5[\alpha\text{-SiW}_{11}\text{NbO}_{40}]\cdot x\text{H}_2\text{O}$, $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$, $K_7[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]\cdot x\text{H}_2\text{O}$ and $K_7[\alpha\text{-SiW}_9\text{Nb}_3\text{O}_{40}]\cdot x\text{H}_2\text{O}$ have been prepared from aqueous solutions of the stable deficient anions $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ and $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$. The compounds have been analyzed by ^{51}V and ^{27}Si MAS NMR. A small distortion was observed at the Si site with tetrahedral coordination after substitution of one or more tungsten atoms by vanadium or niobium in $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$. ^{51}V MAS NMR spectra of $[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]^{7-}$ showed three peaks at -440.2, -492.1 and -532.7 ppm suggesting three different sites in the compound. For $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$, the ^{51}V MAS NMR spectra displayed one peak at -536.2 ppm confirming the presence of a single site. ^{51}V static spectra of $[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]^{7-}$ and $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$ provided anisotropy tensor components characteristic of vanadium in axially distorted octahedral coordination ($\sigma_{11} \approx \sigma_{22} = -326$ ppm $<$ $\sigma_{33} = -933$ ppm and $\Delta\sigma = 450$ -900 ppm). The calculated value of the isotropic shift $\delta_{\text{iso}} = 1/3(2\delta_{\perp} + \delta_{\parallel})$ is 525 ppm for $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$, in agreement with the experimental value of -536.2 ppm.

Resumo: Sais de polioxometalatos mistos com estrutura de Keggin $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, $K_8[\alpha\text{-SiW}_{11}\text{O}_{39}]$, $K_5[\alpha\text{-SiW}_{11}\text{VO}_{40}]\cdot x\text{H}_2\text{O}$, $K_5[\alpha\text{-SiW}_{11}\text{NbO}_{40}]\cdot x\text{H}_2\text{O}$, $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$, $K_7[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]\cdot x\text{H}_2\text{O}$ e $K_7[\alpha\text{-SiW}_9\text{Nb}_3\text{O}_{40}]\cdot x\text{H}_2\text{O}$ foram preparados em solução aquosa dos ânions estáveis lacunares $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ e $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$. Estes compostos foram analisados por MAS RMN de ^{51}V e ^{27}Si . Pequenas distorções foram observadas para o sítio de silício de coordenação tetraédrica depois da substituição de um ou mais átomos de tungstênio pelos átomos de vanádio ou nióbio na estrutura do íon de Keggin $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$. Os espectros de MAS RMN de ^{51}V $[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]^{7-}$ apresentaram três picos em -440,2, -492,1 e -532,7 ppm o que sugere a existência de três sítios diferentes. O espectro de MAS RMN de ^{51}V do íon $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$ apresentou um pico não simétrico em -536,2 ppm confirmando a presença de um único sítio. Os espectros de ^{51}V RMN estático de $[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]^{7-}$ e $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$ forneceram para os componentes do tensor anisotrópico, valores característicos de vanádio em coordenação octaédrica axialmente distorcida ($\sigma_{11} \approx \sigma_{22} = -326$ ppm $<$ $\sigma_{33} = -933$ ppm e $\Delta\sigma = 450$ -900 ppm). O valor calculado do deslocamento isotrópico, $\delta_{\text{iso}} = 1/3(2\delta_{\perp} + \delta_{\parallel})$ foi de 525 ppm para $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$, em boa concordância com o valor de -536,2 ppm obtido experimentalmente.

Introduction

Mixed heteropolyanions of vanadium have been the subject of several studies due to their application in homogeneous and heterogeneous oxidative catalysis.^{1,2} Mixed Keggin compounds $\text{SiW}_{12-x}\text{M}_x\text{O}_{40}$ with $\text{M} = \text{W}$, V or Nb can be obtained from stable tungsten heteropolyanions, $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ and $[\alpha\text{-}$

$\text{SiW}_9\text{O}_{34}]^{10-}$. Figure 1 shows the structure of the Keggin anion where W, V and Nb atoms occupy the center of the octahedron and Si atoms the center of the tetrahedron.³ Three octahedra are connected to form a M_3O_{13} unit with trigonal symmetry. Four M_3O_{13} groups are connected to the vertex of the central heteroatom of Td symmetry in order to form the Keggin structure. The oxygen atoms from

heteropolyanions are classified in four groups, O_a , O_b , O_c e O_d (Figure 1b). O_a is bound to the central atom and to three metal atoms from the M_3O_{13} group while O_b is shared between the metal atoms of two M_3O_{13} units. O_c is bound to two metal atoms from the same M_3O_{13} group and O_d is the terminal oxygen atom bound to only one metal centre.⁴

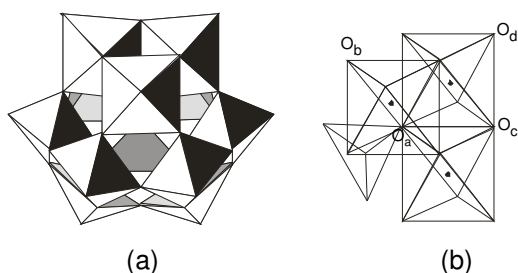


Figure 1. Representation of (a) Keggin anions, $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ and (b) detail of one M_3O_{13} unit connected to XO_4 tetrahedron.

The unsaturated compounds, that is, compounds with a lacunary Keggin structure, are derivatives of $\alpha\text{-SiW}_{12}\text{O}_{40}$ ($\alpha\text{-SiW}_{12}$) formed as a result of the elimination of one MO_6 ($\alpha\text{-SiW}_{11}$) group or loss of three MO_6 octahedra of the same M_3O_{13} ($\alpha\text{-SiW}_9$, B-type) group, or from three different octahedrons ($\alpha\text{-SiW}_9$, A-type). The objective of this work was the synthesis and characterization of several Keggin polyanions using solid state nuclear magnetic resonance.

Experimental

Characterizations.

X-ray diffraction patterns were acquired with a Rigaku – Miniflex diffractometer, applying a 30 kV tension, a 25mA current, using nickel filters and $\text{Cu-K}\alpha$ radiation. Infrared spectra were obtained in the 200 - 4000 cm^{-1} range, using a

Nicolet MAGNA-IR 7600 spectrometer and 0.5 wt.% CsI pellets. The ^{51}V and ^{29}Si NMR spectra were measured using a BRUKER ASX-400 spectrometer (9.4T), with 4 mm and 2.5 mm zirconia rotors for MAS probe. The ^{51}V MAS NMR spectra were performed at spinning speeds of 8 kHz, 10 kHz and 12 kHz. The signal of NaVO_3 (0.16 M aqueous solution) at – 574.28 ppm was used as the reference for the determination of the chemical shift. The ^{29}Si NMR-MAS spectra were done at spinning speeds of 7 kHz and 30 kHz with peak positions referenced to an external standard MTS.

Samples.

All reagents were analytical grade and were used without further purification. The following saturated and unsaturated heteropolyanions salts of Keggin structure were prepared using well known procedures described in the literature^{4,5}, $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]$ and $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$. New synthesis procedures based on the use of niobium oxalate have been proposed to prepare mixed heteropolyanions⁶⁻⁹, $\text{K}_5[\alpha\text{-SiW}_{11}\text{VO}_{40}]$, $\text{K}_5[\alpha\text{-SiW}_{11}\text{NbO}_{40}]$, $\text{K}_7[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]$ and $\text{K}_7[\alpha\text{-SiW}_9\text{Nb}_3\text{O}_{40}]$.

$\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$. IR (cm^{-1}): 1021, 999(sh), 981, 923, 892, 877, 780, 552(sh), 538, 477, 418, 376, 334, 281 and 245.

$\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]$. IR (cm^{-1}): 1002, 968, 900, 867, 798, 725, 624(sh), 534, 513, 474, 419(sh), 367, 334, 278 and 267(sh).

$\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$. IR (cm^{-1}): 985, 940, 930(sh), 865, 804, 694, 556, 526, 500, 485, 436, 371, 332 and 292.

K₅[α -SiW₁₁VO₄₀]: In a beaker, 48.5 mg (0.4 mmol) of sodium metavanadate were dissolved in 10 ml of boiling water under stirring. 1.28 g of solid K₈[α -SiW₁₁O₃₉]·13 H₂O (0.4 mmol) was added to the solution to give an orange solution (pH=6). The heating was switched off but the beaker was left on the hot plate. The pH was adjusted to 7 by addition of a few drops of 6M H₂SO₄. The red solution was kept under stirring for 45 minutes. A precipitate formed slowly and was completed by the addition of 1g of solid KCl. The orange solid was then collected by filtration and dried in air and then recrystallized in hot water. Weight: 0.79g.

IR (cm⁻¹): 995, 961, 906, 974, 975, 528, 475, 368, 333(sh) and 284.

K₅[α -SiW₁₁NbO₄₀]: In a beaker, 1g of K₈[α -SiW₁₁O₃₉], 13 H₂O (0.31 mmol) was dissolved in 20 ml of hot water (45°C) under stirring: Solution A. In another beaker, 0.08 g of K₈Nb₆O₁₉ was totally dissolved in 10 ml of a 0.8M oxalic acid solution. The pH of solution B was then 1.6. Solution B was added to Solution A under stirring. The heating was switched off, but the beaker was left on the hot plate. The pH was adjusted to 6 by addition of solid K₂CO₃. The temperature of the solution was 45°C, and it was kept under gentle stirring for 2h. The volume of the solution was subsequently reduced to 5ml by evaporation. A precipitate started to form, but total evaporation of the solvent was necessary to obtain a white solid which was finally dried in air. Weight: 1.52g.

IR (cm⁻¹): 999, 965, 903, 794, 737, 623(sh), 521, 475, 417, 367, 333 and 278.

K₇[α -SiW₉V₃O₄₀]: In a beaker, 0.16 g (1.33 mmol) of sodium metavanadate was dissolved in 5 ml of boiling water under stirring. 1.21 g of solid Na₁₀[α -SiW₉O₃₄].18.H₂O (0.43 mmol) was added to the solution to give an orange solution. The heating was switched off, but the beaker was left on the hot plate. 1.55 ml of a 6M H₂SO₄ 6M solution was added. The red solution was kept under stirring for 45 minutes. The pH was then adjusted to 6-7 by addition of solid K₂CO₃. An orange precipitate formed after the addition of 0.67g of solid KCl, which was filtered and dried in air. Weight: 0.6g. Yield: 47%.

IR (cm⁻¹): 1113, 981, 956, 906, 884(sh), 793, 749(sh), 616, 527, 465, 375, 336(sh), 279.

K₇[α -SiW₉Nb₃O₄₀]: In a beaker, 1g of Na₁₀[α -SiW₉O₃₄], 18.H₂O (0.36 mmoles) was dissolved in 25 ml of hot water (54°C) under stirring (solution A). In another beaker, 0.27 g of K₈Nb₆O₁₉.x H₂O was totally dissolved at 50°C in 20 ml of a 0.1M oxalic acid (solution B). The pH of solution B was then 5. Solution B was added to solution A under stirring. The heating was switched off, but the beaker was left on the hot plate overnight. A precipitate started to form but total evaporation of the solvent was necessary to obtain a white solid finally dried in air. Weight: 1.28g.

IR (cm⁻¹): 1010, 965, 912, 799(sh), 774, 654(sh), 515, 479(sh), 379, 333, 283 and 244.

Results and Discussion

The salts of [α -SiW₁₂O₄₀]⁴⁻, [α -SiW₁₁O₃₉]⁸⁻ and [α -SiW₉O₃₄]¹⁰⁻ heteropolyanions have been prepared from sodium tungstate Na₂WO₄·2H₂O and sodium metasilicate Na₂SiO₃·H₂O using well-known procedures described in the

literature⁶. New synthesis methods have been used to fill the monolacunary and trilacunary structure, $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ and $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, by vanadium or niobium atoms. On the basis of recent works of Labinger et al.,⁶⁻⁹ we report here a new synthesis procedure using niobium oxalate as a source for incorporating niobium into the lacunary structures $\alpha\text{-SiW}_{11}$ and $\alpha\text{-SiW}_9$. X-ray diffraction powder patterns of all materials were very similar and did not allow differentiation of Keggin compounds. Infrared spectra, however, clearly evidenced the formation of the respective Keggin ions¹⁰⁻¹², $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$, $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ and $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$. The symmetric and asymmetric stretching of the different M-O bands are observed in the following spectral regions: $\nu_{\text{as}}(\text{M-O}_d)$ as a strong band in the $1000\text{-}950\text{ cm}^{-1}$, $\nu_{\text{as}}(\text{M-O}_b\text{-M})$ as a band in the $920\text{-}850\text{ cm}^{-1}$, and $\nu_{\text{as}}(\text{M-O}_c\text{-M})$, as a strong band in about $800\text{-}750\text{ cm}^{-1}$. Table 1 reports the position of the principal bands observed for different compounds. The main stretching bands are characteristic of the Keggin structure.

The ^{29}Si MAS-NMR spectra (Figures 2 and 3) presented narrow peaks in a -86 to -83 ppm range ($\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] = -84.7$ ppm, $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}] = -84.0$, $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}] = -86.0$, $\text{K}_5[\alpha\text{-SiW}_{11}\text{VO}_{40}] = -82.9$ and -83.9 , $\text{K}_5[\alpha\text{-SiW}_{11}\text{NbO}_{40}] = -83.7$, $\text{K}_7[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}] = -82.9$ and $\text{K}_7[\alpha\text{-SiW}_9\text{Nb}_3\text{O}_{40}] = -83.8$). A small distortion was observed at the silicon site of tetrahedral geometry in the $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ anion when vanadium or niobium atoms were substituted for one or more tungsten atoms. Table 2 summarizes the chemical shifts measured for these samples.

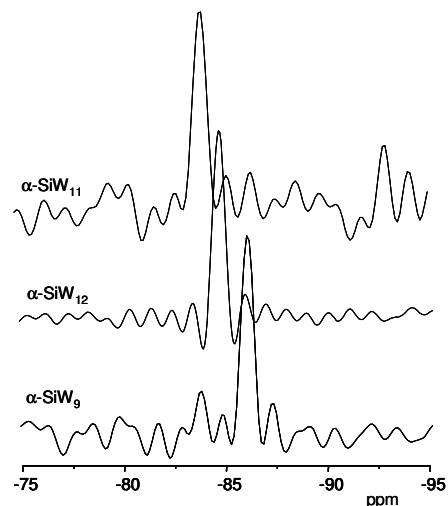


Figure 2. ^{27}Si MAS NMR spectra of $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]$ and $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$.

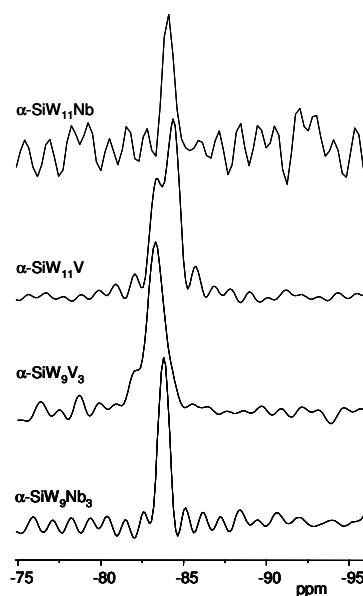


Figure 3. ^{29}Si MAS NMR of $[\alpha\text{-SiW}_{12-x}\text{V}_x\text{O}_{40}]^{n-}$ and $[\alpha\text{-SiW}_{12-x}\text{Nb}_x\text{O}_{40}]^{n-}$ ($x=1$ and 3).

Table 1. Observed frequencies of the IR bands of Keggin ions in the 200-1100 cm^{-1} range and partial assignment.

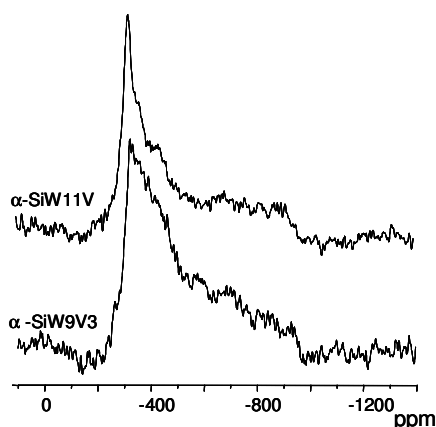
	Compound						
	SiW ₁₂	SiW ₁₁	SiW ₉	SiW ₁₁ V	SiW ₁₁ Nb	SiW ₉ V ₃	SiW ₉ Nb ₃
ν_1	1021					1113	1010
ν_2 M-O _d	999(sh)	1002	985	995	999	981	
ν_3 M-O _d	981	968	940	961	965	956	965
ν_4	923		930 (sh)				
ν_5 M-O _b -M	892	900	865	906	903	906 884(sh)	912
ν_6	877	867(sh)					
ν_7 M-O _c -M	780	798	804	794	794	793	799(sh)
ν_8		730		745	737	749(sh)	774
ν_9		624(sh)	694		623(sh)	616	654 (sh)
ν_{10}	552 (sh)		556				
ν_{11}	538	534	526	528	521	527	
ν_{12}		513	500 485				515
ν_{13}	477	474		475	475	465	479(sh)
ν_{14}			436				
ν_{15}	418	419(sh)			417		
ν_{16}	376	367	371	368	367	375	379
ν_{17}	334	334	332	333(sh)	333	336(sh)	333
ν_{18}	281	278	292	284	278	279	283
ν_{19}	245	267(sh)					244

Table 2. ^{29}Si MAS NMR data for heteropolyanions with Keggin structure.

Compounds	δ_{iso} (ppm)	$\Delta\nu_{1/2}$, Hz
$\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$	-84.7	57
$\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]$	-84.0	63
$\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$	-86.0	58
$\text{K}_5[\alpha\text{-SiW}_{11}\text{VO}_{40}]$	-82.9; -83.9	139
$\text{K}_7[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]$	-82.9	96
$\text{K}_5[\alpha\text{-SiW}_{11}\text{NbO}_{40}]$	-83.7	67
$\text{K}_7[\alpha\text{-SiW}_9\text{Nb}_3\text{O}_{40}]$	-83.8	62

The ^{51}V MAS NMR spectra of $[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]^{7-}$ anion displayed peaks at -440.2; -492.1 and -532.7 ppm, which indicated the presence of three different sites for vanadium in this compound. The ^{51}V MAS NMR spectrum of $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$ anion presented one peak at -536.2 ppm indicating the existence of only one site.

The ^{51}V static spectra of $[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]^{7-}$ and $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$ (Figure 4) showed anisotropic screening tensor values ($\sigma_{11} \approx \sigma_{22} < \sigma_{33}$) typical of distorted octahedral coordination for vanadium.

**Figure 4.** ^{51}V NMR Static spectra of $\text{K}_5[\alpha\text{-SiW}_{11}\text{VO}_{40}]$ and $\text{K}_7[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]$.

They also presented an axial anisotropic screening of $\sigma_{11} \approx \sigma_{22} = -326 \text{ ppm} < \sigma_{33} = -933 \text{ ppm}$ ($\Delta\sigma = 450\text{-}900 \text{ ppm}$). The calculated value^{13,14} ($\delta_{\text{iso}} = 1/3(2\delta_{\perp} + \delta_{\parallel})$) of δ_{iso} was 525 ppm for $[\alpha\text{-SiW}_{11}\text{VO}_{40}]^{5-}$ anion, which is in agreement with the experimental data of -536.2 ppm.

Conclusion

^{29}Si and ^{51}V MAS NMR spectra of $[\alpha\text{-SiW}_9\text{V}_3\text{O}_{40}]^{7-}$ confirmed octahedral coordination of vanadium and formation of mixed Keggin ions by insertion into lacunary tungstosilicates.

Acknowledgments

CAPES-COFECUB / CNPq.

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