Lawrence Berkeley National Laboratory

Recent Work

Title

Multinuclear Solid-State NMR Investigation of Hexaniobate and Hexatantalate Compounds.

Permalink

<https://escholarship.org/uc/item/2q50r5bz>

Journal

Inorganic chemistry, 55(12)

ISSN

0020-1669

Authors

Deblonde, Gauthier J-P
Coelho-Diogo, Cristina
Chagnes, Alexandre
et al.

Publication Date

2016-06-01

DOI

10.1021/acs.inorgchem.6b00345

Peer reviewed

Multinuclear Solid-State NMR Investigation of Hexaniobate and Hexatantalate Compounds

Gauthier J.-P. Deblonde,^{*,†,‡} Cristina Coelho-Diogo,[§] Alexandre Chagnes,[†] Gérard Cote,[†] Mark E. Smith,^{||} John V. Hanna,[⊥] Dinu Iuga,[⊥] and Christian Bonhomme[#]

[†]PSL Research University, Chimie ParisTech-CNRS, Institut de Recherche de Chimie Paris, 11 rue Pierre et Marie Curie, 75005 Paris, France

[‡]ERAMET Research, Hydrometallurgy department, 1 avenue Albert Einstein, F-78193 Trappes, France

[§]Institut des Matériaux de Paris Centre (IMPC-UPMC-FR2482), site collège de France, 75005 Paris, France

^{||}Vice-Chancellor's Office, University House, Lancaster University, Lancaster LA1 4YW, U.K.

[⊥]Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

[#]Sorbonne Universités, UPMC Univ Paris 06, UMR CNRS 7574, Laboratoire de Chimie de la Matière Condensée de Paris, Collège de France, 11 place Marcelin Berthelot, 75005, Paris, France

S Supporting Information

ABSTRACT: This work determines the potential of solid-state NMR techniques to probe proton, alkali, and niobium environments in Lindqvist salts. $\text{Na}_7\text{HNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1), $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2), and $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (3) have been studied by solid-state static and magic angle spinning (MAS) NMR at high and ultrahigh magnetic field (16.4 and 19.9 T). ^1H MAS NMR was found to be a convenient and straightforward tool to discriminate between protonated and nonprotonated clusters $\text{A}_x\text{H}_{8-x}\text{M}_6\text{O}_{19}\cdot n\text{H}_2\text{O}$ (A = alkali ion; M = Nb, Ta). ^{93}Nb MAS NMR studies at different fields and MAS rotation frequencies have been performed on 1. For the first time, the contributions of $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ sites were clearly distinguished from those assigned to NbO_6 sites in the hexaniobate cluster. The strong broadening of the resonances obtained under MAS was interpreted by combining chemical shift anisotropy (CSA) with quadrupolar effects and by using extensive fitting of the line shapes. In order to obtain the highest accuracy for all NMR parameters (CSA and quadrupolar), ^{93}Nb WURST QCPMG spectra in the static mode were recorded at 16.4 T for sample 1. The ^{93}Nb NMR spectra were interpreted in connection with the XRD data available in the literature (i.e., fractional occupancies of the $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ sites). 1D ^{23}Na MAS and 2D ^{23}Na 3QMAS NMR studies of 1 revealed several distinct sodium sites. The multiplicity of the sites was again compared to structural details previously obtained by single-crystal X-ray diffraction (XRD) studies. The ^{23}Na MAS NMR study of 3 confirmed the presence of a much larger distribution of sodium sites in accordance with the 10 sodium sites predicted by XRD. Finally, the effect of Nb/Ta substitutions in 1 was also probed by multinuclear MAS NMR (^1H , ^{23}Na , and ^{93}Nb).

INTRODUCTION

Niobium ($Z = 41$) and tantalum ($Z = 73$) are strategic metals for alloys and the electronic industries and are classified as critical metals due to the few locations where both metals are extracted and because of their use in several applications, including alloys for the automotive, aerospace and nuclear industries, electronic components, superconducting magnets, etc.¹ Whereas classical and economical routes to recover Nb and Ta from natural ores require fluoride media,^{2,3} the development of innovative and sustainable processes to recover Nb and Ta could not be achieved in such media, owing to the environmental and health risks inherent to fluoride solutions. In this regard, alkaline media have recently received growing attention for Nb and Ta recovery, as high solubility of Nb(V)

and Ta(V) can be obtained along with separation from impurities such as Fe, Mn, and Ti.^{4–6}

Niobium and tantalum speciation in alkaline media has been studied since the 19th century⁷ and widely debated during the 20th century, but the chemistry of both group V metals is still challenging and rather unexplored in comparison to other metals such as molybdenum and tungsten and even the lightest group V metal, vanadium. Among a broad variety of polyoxometalates⁸ that can be formed with Nb(V) and Ta(V) in basic media, the Lindqvist salts, namely $\text{A}_x\text{H}_{8-x}\text{Nb}_6\text{O}_{19}\cdot n\text{H}_2\text{O}$ and $\text{A}_x\text{H}_{8-x}\text{Ta}_6\text{O}_{19}\cdot n\text{H}_2\text{O}$ (A = Li, Na,

Received: February 16, 2016

Published: June 1, 2016

K, Rb, Cs, tetramethylammonium, tetrabutylammonium; $0 \leq x \leq 4.5$), are of high importance. Indeed, the Lindqvist ions $H_xNb_6O_{19}^{x-8}$ and $H_xTa_6O_{19}^{x-8}$ are the dominant species of Nb and Ta in aqueous solutions at $pH \geq 10$.^{9,10} Moreover, in the solid state, the Lindqvist salt was the first polyoxoniobate to be isolated and characterized thanks to its stability and relatively easy synthesis.¹¹ The industrial recovery of Nb and Ta by caustic leaching of natural ores was also explained by the formation of the hexameric ions $M_6O_{19}^{8-}$ ($M = Nb, Ta$), highlighting the robustness of the M_6O_{19} framework and its importance in future niobium and tantalum industries.^{12,13}

The structure of the Lindqvist ion M_6O_{19} has been extensively studied and consists of a superoctahedron of 6 edge-sharing and distorted octahedra MO_6 . The M_6O_{19} cluster has 3 different types of oxygen with 1 central μ_6 -O atom inside an M_6O octahedra, 6 $\eta=O$ terminal oxygens, and 12 μ_2 -O bridging oxygens (Figure 1).

Figure 1. Representation of the Lindqvist ion M_6O_{19} (red spheres, oxygen; blue spheres, niobium or tantalum) containing 1 central oxygen (μ_6 -O), 6 terminal oxygens ($\eta = O$), and 12 bridging oxygens (μ_2 -O).

As a consequence of their easy accessibility, most of the studies related to Nb(V) and Ta(V) speciation in alkaline media (in both the solid state and solution) are based on hexaniobate or hexatantalate salts. Although pioneering works were focused on potassium and sodium salts, the chemistry of hexaniobate and hexatantalate salts has recently been extended to their lithium, rubidium, cesium, and quaternary ammonium counterparts (Table 1). Due to the several degrees of freedom that the chemical formula $A_xH_{8-x}M_6O_{19} \cdot nH_2O$ exhibits, an important series of hexaniobate and hexatantalate salts have been reported, even if some of them were not fully characterized.

Even though hexaniobate and hexatantalate salts have been known for a long time, the full resolution of their crystal structure was only performed in the last two decades with important contributions from the Nyman and Hartl groups. For the sodium hexaniobate salt, the structure $Na_7(H_3O)Nb_6O_{19} \cdot 14H_2O$ was first proposed by Goiffon et al. in 1980⁴⁰ and corrected recently to $Na_7H_9Nb_6O_{19} \cdot 15H_2O$ by the Nyman group on the basis of NMR studies (including ^{17}O in the solution state).^{20,36} The very recent advances in the characterization of Nb and Ta Lindqvist salts and other polyoxometalates reflect the complexity of Nb and Ta chemistry and underline the need for developing new techniques to probe such compounds.

Table 1. List of Hexaniobate and Hexatantalate Salts Reported in the Literature^a

compound	space group	ref
$Li_8Ta_6O_{19} \cdot 24H_2O$		14
$Na_6Li(H_3O)Ta_6O_{19} \cdot 14H_2O$	$Pnmm$	15 ^b
$Na_8Ta_6O_{19} \cdot 26H_2O$	$P6_3$ and $R\bar{3}$	16 ^b
$Na_8Ta_6O_{19} \cdot 24.5H_2O$	$P6_3$	17, ^b 18
$Na_8Ta_6O_{19} \cdot 24H_2O$		19
$Na_8Ta_6O_{19} \cdot 15H_2O$	$Pmnn$	19, 20 ^b
$K_7NaTa_6O_{19} \cdot 14H_2O$	$P2_1$	21, ^b 22
$K_8Ta_6O_{19} \cdot 17H_2O$		15, -26
$K_8Ta_6O_{19} \cdot 16H_2O$	Cc	21, ^b 27–30
$K_8Ta_6O_{19} \cdot 12H_2O$		30
$K_8Ta_6O_{19} \cdot 9H_2O$		30
$K_8Ta_6O_{19} \cdot 4H_2O$		30
$Rb_6Na_2Ta_6O_{19} \cdot 21H_2O$	$R\bar{3}$	30 ^b
$Rb_8Ta_6O_{19} \cdot 14H_2O$	$P2_1/n$	31
$Rb_8Ta_6O_{19} \cdot 4H_2O$	$C2/c$	31
$Rb_8Ta_6O_{19}$		31
$Cs_8Ta_6O_{19} \cdot 14H_2O$	$P2_1/n$	31
$Cs_8Ta_6O_{19}$	$I4/m$	31
$TBA_{3.5}[H_{4.5}(Ta_6O_{19})] \cdot 2THF \cdot 5.5H_2O$	$P\bar{1}$	32
$TBA_6H_2Ta_6O_{19} \cdot 10H_2O$	$P2_1/c$	24–33
$Li_8Nb_6O_{19} \cdot 22H_2O$		14
$Li_8Nb_6O_{19} \cdot 15.5H_2O$	$P2_1/c$	34 ^b
$Li_6H_2Nb_6O_{19} \cdot 14H_2O$		34
$KLi_7Nb_6O_{19} \cdot 15H_2O$	$P2_1/n$	20 ^b
$Na_6LiH_9Nb_6O_{19} \cdot 15H_2O$	$Pnmm$	15 ^b
$Na_7H_9Nb_6O_{19} \cdot 15H_2O$	$Pmnn$	18–, ^b 35–40
$Na_7H_9Nb_6O_{19} \cdot 14H_2O$		41
$Na_8Nb_6O_{19} \cdot 13H_2O$		42, 43
$K_4Na_4Nb_6O_{19} \cdot 9H_2O$		43
$K_7H_9Nb_6O_{19} \cdot 16H_2O$		23
$K_7H_9Nb_6O_{19} \cdot 13H_2O$		15, 25, 26, 35–38, 44, 45
$K_7H_9Nb_6O_{19} \cdot 10H_2O$	$C2/c$	46 ^b
$K_8Nb_6O_{19} \cdot 16H_2O$	$C2/c$	46 ^b –48
$K_8Nb_6O_{19} \cdot 10H_2O$		43
$K_6H_2Nb_6O_{19} \cdot 13H_2O$		49, 50
$Rb_8Nb_6O_{19} \cdot 14H_2O$	$P2_1/n$	46 ^b
$Rb_6H_2Nb_6O_{19} \cdot 19H_2O$	$R\bar{3}$	46 ^b
$Rb_6H_2Nb_6O_{19} \cdot 9H_2O$	$P\bar{1}$	46 ^b
$Cs_6Na_2Nb_6O_{19} \cdot 18H_2O$	$R\bar{3}$	46 ^b
$Cs_6H_2Nb_6O_{19} \cdot 9H_2O$	$P2_1/c$ and $Pbca$	46 ^b
$Cs_8Nb_6O_{19} \cdot 14H_2O$	$P2_1/n$	46 ^b
$TMA_5[H_3Nb_6O_{19}] \cdot 20H_2O$	$I2/a$	51 ^b
$TMA_8[Nb_6O_{19}] \cdot 15H_2O$		52
$TBA_4[H_4Nb_6O_{19}] \cdot 7H_2O$		53

^aAbbreviations: TMA, tetramethylammonium; TBA, tetrabutylammonium. ^bThe paper where the crystal structure was solved.

In this regard, solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) seems to be potentially important for studying hexaniobate and hexatantalate salts. In particular, the alkali hexaniobate salts offer a unique class of compounds with multiple nuclei that can be probed by solid-state MAS NMR, namely 1H , 6Li , 7Li , ^{17}O , ^{23}Na , ^{87}Rb , ^{133}Cs , and ^{93}Nb . Although several techniques were used to investigate hexaniobate and hexatantalate salts, only a few articles^{20,36,46,54} have been published on 1H , $^6/7Li$, and ^{93}Nb solid-state MAS

NMR and no ^{23}Na , ^{87}Rb , or ^{133}Cs NMR studies have been performed for such salts to date.

This work underlines the potential of the MAS NMR technique to probe proton, alkali, and niobium environments in Lindqvist salts. The ^1H MAS NMR studies of $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1), $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2), and $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (3) presented in this article illustrate the ability to distinguish between *protonated* and *nonprotonated* clusters with this technique. Under fast MAS (30 kHz), the contribution of the water molecules and $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ groups (if present) to the ^1H MAS or synchronized echo MAS experiments were clearly resolved.

^{93}Nb MAS and static NMR has so far been mainly applied to the characterization of several families of Nb-containing materials,^{54–56} but rarely to hexaniobate salts.⁵⁴ More specifically, *nonprotonated* $[\text{Nb}_6\text{O}_{19}]^{8-}$ clusters in $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ were investigated at ultrahigh magnetic field. In this particular case, three nonequivalent Nb sites were expected on the basis of the crystallographic structure. Nevertheless, all ^{93}Nb static and MAS NMR spectra could be reasonably interpreted with a *unique* set of CSA and quadrupolar parameters (see below). In other words, the spectral resolution was not enough to distinguish all individual ^{93}Nb sites. To the best of our knowledge, no ^{93}Nb NMR parameters have been reported so far for $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ entities and we present here the first complete sets of parameters for such groups. Most importantly, we demonstrate that $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ groups were distinguished on the basis of their characteristic quadrupolar parameters ($C_Q(^{93}\text{Nb})$) and *not* their isotropic chemical shift ($\delta_{\text{iso}}(^{93}\text{Nb})$). The full interpretation of the NMR spectra was related to the corresponding XRD data. Very interestingly, highly resolved ^{23}Na MAS NMR spectra (related to small $C_Q(^{23}\text{Na})$) were sensitive to the small variations in the local order around the sodium atoms. Distributions of $\delta_{\text{iso}}(^{23}\text{Na})$ could be related to order/disorder in the crystallographic structures. The doping of hexaniobate sodium salts with tantalum ($\text{Na}_7\text{HfNb}_{6-x}\text{Ta}_x\text{O}_{19}\cdot 15\text{H}_2\text{O}$ with $x \leq 0.33$) did not significantly influence the ^{93}Nb spectra, whereas ^{23}Na spectra were modified, demonstrating again the particular sensitivity of this technique. The effect of Ta insertion in $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) was finally compared with the crystal structures of the isostructural salts $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) and $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$.

■ EXPERIMENTAL SECTION

Materials. Water used in this study was purified through Millipore DI-pak and Millipore Simpapak2 systems ($R > 18.2 \text{ M}\Omega \text{ cm}$). Acetonitrile (99.9%), NaOH, and KOH were purchased from VWR. Nb_2O_5 (99.9%) and Ta_2O_5 (99.99%) were purchased from Aldrich. NbCl_5 (99%) was purchased from Alfa Aesar.

Synthesis of $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1). A 30.0 g portion of NaOH pellets was finely ground and mixed with 10.0 g of Nb_2O_5 . The mixture was placed in a Pt crucible and heated to 450 °C for 5 h. After the mixture was cooled to room temperature, the calcinate was successively washed with $2 \times 250 \text{ mL}$ and $3 \times 100 \text{ mL}$ of water. The solid was then recrystallized as follows. About 20 g of solid was dissolved in 300 mL of water at $\sim 90^\circ\text{C}$. After hot filtration, the filtrate was gently cooled to room temperature so that, after about 2 h, fine crystals appeared on the walls and at the bottom of the chiller. The colorless crystals were recovered by Büchner filtration and washed with 20 mL of water and 20 mL of absolute ethanol. The crystals were then dried in air for 48 h. SEM images of crystals 1 are given in Figure S1 in the Supporting Information. In order to check the elimination of NaOH excess, required by the alkaline fusion, the Nb/Na ratios were measured by ICP-AES at the different steps of the synthesis. This yielded a Na/Nb molar ratio of >10000 (washing 1), 23.9 (washing 2),

2.83 (washing 3), 1.80 (washing 4), 1.82 (washing 5), 1.17 (recrystallization filtrates) and 1.17 (salt). The product was identified as $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ by powder X-ray diffraction and Raman and infrared spectroscopy. The yield was 38% based on Nb. Anal. Calcd for $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$: H₂O, 20.9; Na, 12.4; Nb, 43.1. Found: H₂O, 21.5; Na, 12.0; Nb, 41.6. Raman (cm^{-1}): 904, 837, 769, 524, 485, 458, 380, 278, 215, 172. IR (cm^{-1}): 3226 (vs), 1658 (m), 1631 (m), 847 (s), 756 (s), 692 (vs), 617 (s). The Raman spectrum and TGA analyses are given in Figures S2 and S3 in the Supporting Information.

Synthesis of $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2). In this contribution, sample 2 will be of particular help for the interpretation of ^1H MAS NMR spectra (see below). This compound was synthesized starting from NbCl_5 , as detailed elsewhere.⁹ $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ was identified by powder X-ray diffraction and Raman and infrared spectroscopy. Anal. Calcd for $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$: H₂O, 19.7; K, 21.4, Nb, 38.1. Found: H₂O, 19.6; K, 20.7; Nb, 36.2. Raman (cm^{-1}): 875, 827, 745, 530, 459, 376, 288, 217. IR (cm^{-1}): 3222 (vs), 1653 (m), 1631 (m), 847 (s), 697 (vs), 617 (m). The Raman spectrum and TGA analyses are given in Figures S4 and S5 in the Supporting Information.

Synthesis of $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (3). The synthesis was inspired by the method of Abramov et al.¹⁷ A 5.9 g portion of NaOH pellets was finely ground and mixed with 3.3 g of Ta_2O_5 . The mixture was placed in a Pt crucible and heated to 450 °C for 5 h. The purification of the calcinate was performed similarly to the $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ synthesis. SEM images of 2 crystals are given in Figure S6 in the Supporting Information. The yield was 44% based on Ta. Anal. Calcd for $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$: H₂O, 21.9; Na, 9.1; Ta, 53.9. Found: H₂O, 22.0; Na, 8.9; Ta, 51.9. Raman (cm^{-1}): 861, 754, 511, 420, 346, 213, 187, 172. IR (cm^{-1}): 3226 (vs), 1657 (m), 831 (s), 767 (s), 692 (vs), 617 (s). The Raman spectrum and TGA analysis are given in Figures S7 and S8 in the Supporting Information.

Solid-State MAS NMR at High and Ultrahigh Magnetic Field.

Solid-state NMR experiments were performed on the following: (i) a Bruker AVANCE III 700 spectrometer at 16.4 T ($\nu_0(^1\text{H}) = 700 \text{ MHz}$, $\nu_0(^{23}\text{Na}) = 185.22 \text{ MHz}$, $\nu_0(^{93}\text{Nb}) = 171.39 \text{ MHz}$) with 2.5 mm (30 kHz) and 1.3 mm (65 kHz) double-resonance Bruker MAS probes and 5 mm Bruker static probe and with samples spun at the magic angle using ZrO_2 rotors; (ii) a Bruker AVANCE II 850 spectrometer at 19.9 T ($\nu_0(^1\text{H}) = 850 \text{ MHz}$, $\nu_0(^{23}\text{Na}) = 224.91 \text{ MHz}$, $\nu_0(^{93}\text{Nb}) = 208.12 \text{ MHz}$) with a 1 mm (80 kHz) double-resonance Jeol MAS probe. ^1H MAS spectra were obtained by using a single pulse experiment (SPE) ($t_{90}(^1\text{H}) = 3.0 \mu\text{s}$ for the 2.5 mm MAS probe) and synchronized Hahn echo for spectral editing (two-pulse sequence: $p_1 - \tau - p_2$ with $p_1 = 3.0 \mu\text{s}$ and $p_2 = 6.0 \mu\text{s}$ and with a 16-step phase cycling). The longest interpulse delay corresponded to 10 rotor periods. For quantitative purposes, all 1D ^{23}Na ($I = 3/2$) MAS NMR spectra were obtained by using short pulses ($< \pi/8$). Nutation curves were first established by using a solution of 1 M NaCl(aq) ($t_{90}(^{23}\text{Na}) = 8.8 \mu\text{s}$ for the 2.5 mm MAS probe). ^{93}Nb WURST QCPMG⁵⁷ spectra were obtained by using a 5 mm static probe. As the sensitivity of the experiment was high, no DFS enhancement technique⁵⁸ was implemented. The WURST shape was defined as follows: sweep width of 1000 kHz (during 45 μs), definition by 1000 points. The power of the rf field was then the only optimized parameter (here, $\sim 10 \text{ W}$). Probe contributions to the final signals were carefully checked under the same experimental conditions. Finally, potential effects of the irradiation offset for ^{93}Nb were explored as well (see Results and Discussion). 2D ^{23}Na 3QMAS NMR spectra⁵⁹ were obtained by using an amplitude modulated Z-filter experiment ($p_1 - t_1(3\text{Q evolution}) - p_2 - \tau - p_3 - t_2(\text{acquire})$).⁶⁰ The optimized pulse lengths of the 3Q excitation (p_1) and reconversion (p_2) were $p_1 = 4.0 \mu\text{s}$ and $p_2 = 2.0 \mu\text{s}$, respectively, implemented with an rf field of 85 kHz, whereas the soft $\pi/2$ Z-filter (p_3) was set to 40 μs , which was delivered with an rf field of $\sim 3 \text{ kHz}$. Synchronized echoes (the interpulse delay was always set to one rotor period) with short pulses ($\pi/10$) were used as well for ^{93}Nb ($I = 9/2$) MAS NMR ($t_{90}(^{93}\text{Nb}) = 4.0 \mu\text{s}$ for a saturated solution of NbCl_5 in acetonitrile using the 1.3 mm MAS probe and $t_{90}(^{93}\text{Nb}) = 12.0 \mu\text{s}$ for the 2.5 mm MAS probe). As protons are present in all structures, a systematic investigation of the effects of $\{^1\text{H}\}$ decoupling on ^{23}Na and ^{93}Nb spectra was performed. Tiny

effects on spectral resolution were observed, so that mainly undecoupled ^1H spectra were recorded in this study. In terms of ^1H homonuclear decoupling, and in order to further increase the ^1H spectral resolution, an optimized DUMBO (decoupling using mind-boggling optimization) sequence was implemented at lower MAS frequency (12 kHz).⁶¹ No increase in resolution was observed for compounds 1–3.

^1H and ^{23}Na NMR chemical shifts were referenced to TMS (tetramethylsilane) (via solid adamantane) and a 0.1 M solution of $\text{NaCl}_{(\text{aq})}$, respectively. As a convenient secondary chemical shift reference, a powder sample of NaCl was also used (+7.25 ppm). ^{93}Nb NMR chemical shifts were referenced to a saturated solution of NbCl_5 in acetonitrile at 0.0 ppm. Lapina et al.⁵⁴ used this reference, whereas Hanna et al.⁵⁵ used the following solution as a chemical shift reference: $\text{K}[\text{NbCl}_6]/\text{CH}_3\text{CN}$. A solution of NbCl_5 in acetonitrile without KCl exhibits three peaks. The most deshielded peak is sharp, the second peak is broader and is shifted by about -55 ppm, and the third peak is sharp and shifted by about -494 ppm. The second peak disappears after several hours. These three peaks were attributed to the equilibrium among NbCl_5 , NbCl_6^- , and NbCl_4^+ . The value of 0 ppm was attributed to the most deshielded peak (i.e., NbCl_6^-). All MAS experiments were performed without any temperature control of the samples. The expected increase in temperature was the following: $T_{\text{sample}} \approx 45$ °C for a 2.5 mm probe at 30 kHz and 40 °C for a 1.3 mm probe at 65 kHz.

All decompositions of spectra were performed using the DMfit software, available free of charge online.⁵⁴ For ^1H spectra, Lorentz/Gaussian (L/G) line shapes were used. For ^{23}Na spectra, the $Q_{\text{mas}}/2$ option was used corresponding to the central transition (broadened by eventual second-order quadrupolar effects) under the assumption of infinite MAS rotation frequency (no spinning sidebands). For ^{93}Nb , previous studies have clearly demonstrated the combined role of quadrupolar interaction and CSA on the line shapes, especially at high magnetic field.^{54,55} Consequently, the *int2QUAD* DMfit module was used under the assumption of finite rotation frequency for the central transitions. In order to accurately quantify the spectra, the contribution of the satellites was taken into account in the region of the central transition resonances (the corresponding line shapes were obtained far from the isotropic regions of interest, where the contributions of the spinning sidebands of the central transitions are negligible). The following parameters were taken into account for each ^{93}Nb site: $\delta_{\text{iso}}(^{93}\text{Nb})$, CSA (including the anisotropy, δ_{CSA} , and the asymmetry, η_{CSA}), $C_Q(^{93}\text{Nb})$, $\eta_Q(^{93}\text{Nb})$, and the set of Euler angles between both tensors. The following conventions held.⁶² The electric field gradient (EFG) was characterized by V_{xx} , V_{yy} , and V_{zz} with $|V_{yy}| \leq |V_{xx}| \leq |V_{zz}|$ and $V_{xx} + V_{yy} + V_{zz} = 0$, $C_Q = eQV_{zz}/h$, and $\eta_Q = (V_{yy} - V_{xx})/V_{zz}$ with $0 \leq \eta_Q \leq 1$. CSA was characterized by δ_{11} , δ_{22} , and δ_{33} with $|\delta_{33} - \delta_{\text{iso}}| > |\delta_{11} - \delta_{\text{iso}}| > |\delta_{22} - \delta_{\text{iso}}|$, $\delta_{\text{iso}} = 1/3(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{\text{CSA}} = \delta_{33} - \delta_{\text{iso}}$ (anisotropy), and $\eta_{\text{CSA}} = |(\delta_{22} - \delta_{11})/\delta_{\text{CSA}}|$ (asymmetry). The set of Euler angles $\{\varphi, \chi, \Psi\}$ oriented the CSA tensor in the quadrupolar tensor principal axis system. Full experimental details (e.g., rotor diameter ϕ , MAS frequency ν_{rot} , number of scans NS, recycle delay RD, line broadening LB) are systematically shown in the figure captions.

RESULTS AND DISCUSSION

^1H MAS NMR. The three different Lindqvist salts $\text{Na}_7\text{HNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (1), $\text{K}_8\text{Nb}_6\text{O}_{19} \cdot 16\text{H}_2\text{O}$ (2), and $\text{Na}_8\text{Ta}_6\text{O}_{19} \cdot 24.5\text{H}_2\text{O}$ (3) were investigated by 1D ^1H MAS NMR. The sodium hexaniobate salt 1 has 15 water molecules surrounding the Nb_6O_{19} cluster and only one proton bound to the cluster by one bridging oxygen $\mu_2\text{-O}$ ($\text{NbO}_5\text{O}_{\mu_2}\text{H}$ site) (Figure 1). The structure of 1 was extensively studied by Alam et al.³⁶ using ^1H MAS, ^1H – ^{93}Nb TRAPDOR (transfer of population in double resonance),⁶³ and solution-state ^{17}O NMR experiments. The ^1H MAS NMR spectrum of 1 has a sharp peak at +1.9 ppm and a much broader broad peak centered at +6.3 ppm (Figure 2), in agreement with Alam et al.

Figure 2. ^1H MAS and Hahn echo MAS NMR spectra of $\text{Na}_7\text{HNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (1). See Table S1 in the Supporting Information for NMR parameters. Vertical dashed lines are guides for the eye only (showing the complexity of the broad line centered at +6.3 ppm).

The large peak at +6.3 ppm was assigned to the water molecules and the sharp peak at +1.9 ppm to the proton bound to $\text{NbO}_5\text{O}_{\mu_2}\text{H}$ sites. The Nb–OH resonance is strongly shielded as a consequence of the geometry of the local H-bond networks.⁶⁴ Indeed, the variation of $\delta_{\text{iso}}(^1\text{H})$ could be easily related to the minimum $\text{OH} \cdots \text{O}$ distance with the following rule: $\delta_{\text{iso}}(^1\text{H})$ decreased strongly upon increasing the $\text{OH} \cdots \text{O}$ distance. In other words, protons in Nb–OH groups are rather isolated, leading to the net shielding of $\delta_{\text{iso}}(^1\text{H})$ in comparison to protons in water molecules.

Using a Hahn echo MAS NMR experiment (Figure 2), it was possible to clearly distinguish the $\text{NbO}_5\text{O}_{\mu_2}\text{H}$ resonance by $T_2(^1\text{H})$ filtering. This allowed the extraction of precise line shapes and $\delta_{\text{iso}}(^1\text{H})$ values for the whole ^1H spectrum. It has to be noted that the broad OH resonance is actually much more complex than a simple Lorentzian line shape. It corresponds probably to the sum of individual components with variable $T_2(^1\text{H})$. It follows that accurate quantification of the two components ($\delta_{\text{iso}}(^1\text{H}) = +6.3$ and $+1.9$ ppm) was difficult to obtain. Nevertheless, this simple approach is sufficient to distinguish between $\text{NbO}_5\text{O}_{\mu_2}\text{H}$ group and water molecule resonances. We finally mention that this analysis is in agreement with results already published by Alam et al.³⁶ The authors used $T_2(^1\text{H})$ -based editing techniques as well as double-quantum filtering to achieve realistic assignments. We further observe that spinning faster at the magic angle (>30 kHz) did not lead to a significant increase in resolution, demonstrating that for $30 \text{ kHz} \leq \nu_{\text{rot}}$ ^1H – ^1H homonuclear dipolar couplings were efficiently averaged, leaving only isotropic ^1H chemical shift distributions (mainly related to protons in water molecules).

In order to further compare protonated and nonprotonated clusters, solid-state ^1H NMR spectra of 2 and 3 were recorded (Figure 3). The ^1H NMR peaks related to the water molecules present in 2 and 3 are much sharper in comparison to the broad peak found for $\text{Na}_7\text{HNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (1). Moreover, no shielded resonance (<2 ppm) was observed for these derivatives. In contrast to the case for the alkali hexaniobate salts, no protonated hexatantalate alkali salts have been reported so far (see Table 1). This is mainly due to the lower pK_a of the couple $\text{HTa}_6\text{O}_{19}^{7-}/\text{Ta}_6\text{O}_{19}^{8-}$ in comparison to

Figure 3. ^1H MAS NMR spectra of $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2) (black) and of $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (3) (red). See Table S1 in the Supporting Information for NMR parameters.

$\text{HNb}_6\text{O}_{19}^{7-}/\text{Nb}_6\text{O}_{19}^{8-}$.^{10,22} Consequently, the rather sharp ^1H peak observed for 3 cannot arise from protons linked to the hexatantalate cluster. The similarity between the ^1H NMR spectra of $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2) and $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (3) also suggested that a sharp H_2O peak at ~ 4.5 ppm was only obtained for nonprotonated salts. It is also interesting to note that Nyman et al.⁴⁶ mentioned that ^1H MAS NMR spectra of the protonated salts $\text{Rb}_6\text{H}_2\text{Nb}_6\text{O}_{19}\cdot 9\text{H}_2\text{O}$ and $\text{Cs}_6\text{H}_2\text{Nb}_6\text{O}_{19}\cdot 9\text{H}_2\text{O}$ also exhibited a broad resonance around +5 ppm related to water molecules. The broad resonance at around +5 ppm was also observed by Alam et al.⁶⁵ for the protonated slats $\text{Rb}_6(\text{H}_3\text{O})_2\text{Nb}_6\text{O}_{19}\cdot 17\text{H}_2\text{O}$ and $\text{K}_7\text{HNb}_6\text{O}_{19}\cdot 10\text{H}_2\text{O}$. To our knowledge, no ^1H NMR spectra of the water molecules of fully deprotonated hexaniobate or hexatantalate clusters have been reported in the literature. The observation of a rather sharp H_2O peak for 2 and 3 could suggest that the water molecules are subjected to local motion in their crystal lattice. As a consequence, the ^1H – ^1H homonuclear dipolar interactions are partially averaged at room temperature, leading to much sharper ^1H resonances. NMR spectra presented in Figure 3 suggest that the H_2O molecules in 2 and 3 are not all equivalent. On the basis of the available XRD data, six water molecules are expected in the asymmetric unit of 2. In the case of 3, the positions of the water molecules are not located in the published XRD structure but several nonequivalent water molecules are expected, given the complex structure of this compound (see Na MAS NMR). Attempts to improve the resolution of the ^1H signal by DUMBO acquisition (see the Experimental Section) did not lead to significant improvement in the spectral resolution (the DUMBO sequence promotes efficient averaging of the strong ^1H – ^1H homonuclear couplings). It is assumed here that local motion of the protons drastically lowered the efficiency of the DUMBO sequence. Moreover, an interesting correlation could be established between the ^1H MAS NMR spectra and the TGA of samples 1–3) (see the Supporting Information for TGA curves). In the case of 1, water protons (and $\text{NbO}_5\text{O}_{\mu 2}\text{H}$) participate in a rather rigid H-bond network, as shown by the broad ^1H resonance at +6.3 ppm. On the TGA curve, the loss of almost all water molecules was observed at $T \approx 125$ °C. It is expected from Figure 3 that partial averaging of the ^1H – ^1H homonuclear dipolar interaction should lead to a less rigid H-bond network. Indeed, the loss of water molecules occurred at lower T (~ 90 °C) for 2 and 3. Rather unexpectedly, the global ^1H line widths for 2 and 3 were comparable, indicating similar proton local dynamics in both samples. However, we stress the fact that the average proton chemical shifts for 2 and 3 were clearly separated (difference of ~ 0.75 ppm). This demonstrated the

extreme sensitivity of this particular NMR parameter toward the chemical nature of the metal in the oxo clusters and the alkaline counteranion. It follows that $\delta_{\text{iso}}(^1\text{H})$, though averaged through dynamic processes, should be a pertinent indicator for a detailed analysis of metal derived oxo clusters.

The use of ^1H MAS and Hahn echo MAS NMR for identification of protonated or deprotonated hexaniobate and hexatantalate salts is straightforward in comparison to other techniques such as Raman spectroscopy.⁶⁶ Due to the variety of the hexametalate salts that have been reported in the literature (see Table 1) and the difficulty in identifying the protonation state of such salts, fast MAS NMR represents a powerful tool which can supplement the bond-valence sum (BVS) calculations or bond length examinations traditionally used to rule out the presence of protons bound to the cluster.

^{93}Nb Echo MAS NMR. ^{93}Nb is another nucleus found in hexaniobate salts that can be probed by solid-state NMR. Thanks to its natural abundance (100%) and its relatively high content in hexaniobate salts (~ 25 – 50 wt %), ^{93}Nb MAS NMR spectra with good signal to noise ratio can be obtained in only a few hours. Nonetheless, ^{93}Nb has a high nuclear spin ($I = 9/2$) and a large quadrupole moment (-0.32 barn), which complicate the use of NMR techniques to study this particular nuclei.

Most of the works published on ^{93}Nb MAS NMR were performed on niobium oxides⁵⁵ or mixed-metal oxides that are used as catalysts, piezoelectric components, or optoelectronic materials.^{54,67–71}

To the best of our knowledge, the only ^{93}Nb static/MAS NMR study performed on a hexaniobate salt has been reported recently by Lapina et al.⁵⁴ On the basis of the reported crystallographic structure,⁴⁶ together with the static and MAS NMR spectra recorded at high magnetic field (21.1 T), the ^{93}Nb NMR parameters of $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2) were determined. The authors reported that the three nonequivalent niobium sites present in 2 were practically indistinguishable and that their NMR frequencies could almost be described by a unique ^{93}Nb site with $\delta_{\text{iso}}(^{93}\text{Nb}) = -920$ ppm, $C_Q = 42$ MHz, and $\eta_Q = 0.0$. The authors also revealed that the calculated NMR parameters ($\delta_{\text{iso}}(^{93}\text{Nb})$) for the cluster $\text{Nb}_6\text{O}_{19}^{8-}$ surrounded by eight K^+ ions did not significantly differ from the NMR parameters calculated for $\text{Nb}_{10}\text{O}_{28}^{6-}$ surrounded by six protons. In other words (and mainly on the basis of ab initio calculations), it seemed difficult to distinguish $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ from NbO_6 groups by relying only on isotropic chemical shift. We studied here $\text{Na}_7\text{HNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) by ^{93}Nb echo MAS NMR. Even when very fast MAS at ultrahigh magnetic fields was used, the approximation of infinite MAS rotation frequency did not apply here. Indeed, spinning sidebands of central transitions were clearly observed (see Figure 4).

In contrast with the difficulty in resolving the three different Nb sites found in $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$,⁵⁴ the spectra obtained for $\text{Na}_7\text{HNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) could be reasonably simulated by using two distinct line shapes broadened by second-order quadrupolar and CSA effects. The starting values for the NMR parameters were first determined using the spectrum exhibiting the most significant discontinuities (i.e., $\nu_{\text{rot}} = 65$ kHz, 700 MHz, see Figure 4A). As CSA and second-order quadrupolar effects have an opposite dependence on B_0 , the parameters were further refined at higher field (850 MHz) (Figure 4C) (and also by varying ν_{rot} ; see Figure 4B). The optimized ^{93}Nb NMR parameters all derived from echo MAS NMR experiments are presented in Table 2. These results confirmed the

Figure 4. ^{93}Nb echo MAS NMR spectra of $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (**1**): (A) (dashed lines) simulations using DMfit⁶² and the NMR parameters given in Table 2 (site 1, green; site 2, purple; sum, red solid line), (black solid line) experimental spectrum, (vertical gray arrows) spinning sidebands of the central transitions (CT), and an insert giving a simulated red line (sum of sites 1 and 2) corresponding to CT broadened by second-order quadrupolar effects *only* (see main text); (B) (dashed lines) simulations using the NMR parameters given in Table 2 (site 1, green; site 2, purple; sum, red solid line) and (black solid line) experimental spectrum, with isotropic parts and spinning sidebands (SSBs) of the CT superimposed here; (C) (dashed lines) simulations using the NMR parameters given in Table 2 (site 1, green; site 2, purple; sum, red solid line), (black solid line) experimental spectrum, and (vertical gray arrows) spinning sidebands of the central transitions (CT). See Table S1 in the Supporting Information for NMR parameters.

previously reported crystallographic structure determined by single-crystal X-ray diffraction studies,²⁰ as two groups of Nb atoms are indeed expected (protonated sites, $\text{NbO}_5\text{O}_{\mu 2}\text{H}$; nonprotonated sites, NbO_6).

Several comments can be made on the simulations presented in Figure 4. (i) The extracted $\delta_{\text{iso}}(^{93}\text{Nb})$ values are comparable for Nb sites 1 and 2, whereas they can be clearly distinguished by their respective C_Q values. It follows that both sites were distinguished best at the *lowest* magnetic field (as second-order quadrupolar effects are then dominant). We stress that the observed $\delta_{\text{iso}}(^{93}\text{Nb})$ values for **1** were in agreement with data already published in the literature for niobium oxides,^{54,55} (ii) CSA effects have to be taken into account for accurate simulations. In the absence of such interactions, the spinning sidebands associated with the central transitions are clearly underestimated (see the inset in Figure 4A). The intensities of the first sidebands of the central transitions were very useful for the determination of δ_{CSA} and $\{\varphi, \chi, \Psi\}$ Euler angles. Again we stress the fact that the extracted δ_{CSA} values were comparable to published data.^{54,55} (iii) The clear separation of central transitions from the corresponding spinning sidebands is achieved at ultrafast MAS. At moderate MAS (30 kHz; see Figure 4B), all contributions are superimposed. Nevertheless, such spectra remain useful for further refinement of the parameters presented in Table 2. (iv) Accurate integration of the lines has to take into account the central transitions *and* the associated spinning sidebands. The ratio $\sim 1:2$ is obtained for site 1:site 2. From MAS experiments, the following ^{93}Nb NMR parameters were extracted as first reasonable estimations: site 1, $\delta_{\text{iso}} = -890$ ppm, $\delta_{\text{CSA}} = +550$ ppm, $\eta_{\text{CSA}} = 1$, $C_Q = 33.0$ MHz, $\eta_Q = 0.3$, $\{\varphi, \chi, \Psi\} = \{0, 50, -30\}^\circ$; site 2, $\delta_{\text{iso}} = -880$ ppm, $\delta_{\text{CSA}} = +650$ ppm, $\eta_{\text{CSA}} = 1$, $C_Q = 55.0$ MHz, $\eta_Q = 0.5$, $\{\varphi, \chi, \Psi\} = \{70, 90, 0\}^\circ$. In order to further validate ^{93}Nb CSA parameters and Euler angles, static experiments were performed at 16.4 T. It is indeed established that such experiments should help for an even more accurate determination of these parameters. From an NMR point of view, this can be considered as a challenge, since C_Q for both sites can be considered as large or very large leading to (i) a strong broadening of the static line shapes and (ii) a dramatic decrease in the signal to noise ratio. In order to circumvent this particular problem, the WURST QCPMG⁵⁷ approach was implemented successfully. The efficiency of the WURST excitation was carefully checked by variable offset experiments. It was clearly demonstrated that a *single* offset experiment was sufficient to obtain an undistorted line shape for **1**. Indeed, variations of the offset (± 150 kHz) showed no significant variations of the global spikelet intensities. The ^{93}Nb WURST QCPMG spectra of **1** and commercial NaNbO_3 are presented in Figure S9 in the Supporting Information. NaNbO_3 was used here as a reference compound with $C_Q \approx 20$ MHz.⁵⁵ The corresponding simulation obtained by using parameters already reported by Hanna et al.⁵⁵ is in very good agreement with the envelope of the spikelets. The spectrum of **1** is characterized by a broad and complex line shape. Nevertheless, it exhibits clear discontinuities which are related to the subtle interplay between CSA and quadrupolar tensors (through Euler angles for both sites 1 and 2). Despite the intrinsic complexity of the spectrum, a two-site simulation could be safely derived starting from the data derived from MAS experiments (see above). Most importantly, it was demonstrated that the final line shape was highly sensitive to small variations of the NMR parameters. As a representative example, the strong influence of the Euler angle χ for site 1 is presented in Figure S9. It follows that accurate NMR parameters could be finally extracted for sites 1 and 2: they are summarized in Table 2.

Table 2. ^{93}Nb NMR Parameters Determined for $\text{Na}_7\text{HNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1)^a

	δ_{iso} (ppm)	C_Q (MHz)	η_Q	δ_{CSA} (ppm)	η_{CSA}	$\{\varphi, \chi, \Psi\}$ (deg)	integration (%)
site 1	−890	35.0	0.3	+550	0.95	$\{0 \pm 5, 42 \pm 2, -20 \pm 5\}$	~34
site 2	−880	56.5	0.9	+650	0.95	$\{105 \pm 3, 78 \pm 2, 26 \pm 6\}$	~66

^aSee also Figure 4. Parameters were extracted by using DMfit⁶² and simulations at variable magnetic field and ν_{rot} and under static mode (see Figure S9 in the Supporting Information). The definitions of all parameters are given in the Experimental Section. Site 1: $\text{NbO}_5\text{O}_{\mu 2}\text{H}$. Site 2: NbO_6 (based on integration of the lines; see main text). δ_{iso} values are ± 10 ppm, C_Q values are ± 0.5 MHz, η_Q values are ± 0.1 , δ_{CSA} values are ± 15 ppm, and η_{CSA} values are ± 0.05 .

Figure 5. ^{23}Na MAS NMR spectrum of $\text{Na}_7\text{HNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1). Insert: ^{23}Na 3QMAS NMR spectrum. The simulated NMR parameters for #1–#7 are given in Table 3. See Table S1 in the Supporting Information for NMR parameters.

In contrast to the case for $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2), $\text{Na}_7\text{HNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) exhibits one proton bound to one bridging oxygen ($\text{Nb}-\text{OH}-\text{Nb}$) (Figure 1). This yields a unique situation where Nb atoms in the Nb_6O_{19} moiety readily have two different environments. Indeed, when the Nb_6O_{19} cluster is fully deprotonated, there are only minor differences between the Nb sites which renders their NMR signatures very difficult to distinguish, as already reported for $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2).⁵⁴ Similarly, if more than one proton is bound to Nb_6O_{19} , several isomers could be formed which would render the NMR study more complex. The ^{93}Nb chemical shifts observed for 1 are in the range of what is expected for the distorted NbO_6 and $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ octahedra. For comparison, the $\delta_{\text{iso}}(^{93}\text{Nb})$ values reported⁵⁴ for $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ range from −772 to −920 ppm (including here experimental and ab initio computed parameters). As already stated above, $\delta_{\text{iso}}(^{93}\text{Nb})$ was not able to distinguish NbO_6 from $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ sites. However, $C_Q(^{93}\text{Nb})$ parameters allowed an assignment for niobium sites 1 and 2 to be proposed on the basis of point iv above. Following the ~1:2 ratio, the line with the smaller $C_Q(^{93}\text{Nb})$ value (33.0 MHz; see Table 2) was assigned to $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ (two sites per Nb_6O_{19} cluster), whereas the larger

$C_Q(^{93}\text{Nb})$ value (55.0 MHz) is assigned to NbO_6 (four sites per Nb_6O_{19} cluster). We stress here that the $Pmnn$ space group for 1²⁰ led to the presence of four $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ sites per Nb_6O_{19} cluster due to symmetry operations but only two of them were present from a stoichiometric point of view. It follows that some distribution should be expected for the chemical environment of the Nb atoms. Such distributions were clearly not detected by ^{93}Nb MAS NMR, as only two sets of NMR parameters were indeed sufficient for the accurate description of the spectra (Table 2). This point is also discussed in the context of the ^{23}Na MAS and 3QMAS NMR data. We close this section by mentioning that some authors have applied the concept of local distortion around a given quadrupolar nucleus in order to interpret the magnitude of C_Q .^{72,73} Such distortions are characterized by the so-called strain ($|\Psi|$) and longitudinal strain ($|a|$) parameters (calculated from experimental bond angles and bond lengths). Unfortunately, Hanna et al.⁵⁵ demonstrated very nicely that no clear correlation could be established between $|\Psi|$ and/or $|a|$ and $C_Q(^{93}\text{Nb})$. In other words, such an approach did not allow for the assignment of Nb_5OH and NbO_6 sites on the basis of the effects of local geometry on $C_Q(^{93}\text{Nb})$.

^{23}Na MAS NMR. As a result of its natural abundance (100%), ^{23}Na ($I = 3/2$) is a very amenable nucleus for NMR study, so that ^{23}Na MAS NMR has proven to be an efficient tool to characterize polyoxometalates such as $\text{Na}_6\text{P}_2\text{Mo}_5\text{O}_{23} \cdot 7\text{H}_2\text{O}$ and $\text{Na}_{15}(\text{PO}_3)_3\text{PNb}_9\text{O}_{34} \cdot 22\text{H}_2\text{O}$.^{41,74} Nonetheless, ^{23}Na NMR has never been used to investigate hexaniobate or hexatantalate salts (to the best of our knowledge). Here we probed $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (**1**) and $\text{Na}_8\text{Ta}_6\text{O}_{19} \cdot 24.5\text{H}_2\text{O}$ (**3**) by ^{23}Na solid-state 1D MAS and 3Q MAS NMR.

The 1D and 2D ^{23}Na NMR spectra of **1** are given in Figure 5. Fast MAS at 40 kHz led to a very well resolved spectrum exhibiting several overlapping resonances. We stress here that, when ν_{rot} is increased to 65 kHz, small continuous variations of some $\delta_{\text{iso}}(^{23}\text{Na})$ values (<0.3 ppm) were observed. Such variations were fully reversible by lowering ν_{rot} and could be interpreted in terms of local heating of the sample due to friction of the rotor at the highest rotation frequencies.

The 1D ^{23}Na fast MAS spectrum was simulated by using information extracted from the 3QMAS experiment (see the inset in Figure 5 and Table 3). In order to quantify the various

Table 3. ^{23}Na NMR Parameters Determined for $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (**1**)^a

site	δ_{iso} (ppm)	C_Q (MHz)	η_Q	integration (%)
#1	−1.30	2.07	0.75	21
#2	+0.90	1.95	0.90	19
#3	+5.20	1.32	0.60	~2
#4	+4.20	<0.03		25
#5	+6.80	<0.03		12
#6	+9.30	<0.03		14
#7	+9.00			7

^aSee also Figure 5. Parameters were extracted by using DMfit.⁶² The definitions of all parameters are given in the Experimental Section. The various peaks are labeled as follows (see Figure 5): #1–#3, second-order quadrupolar broadened line shapes (central transitions); #4–#6, Lorentz/Gauss line shapes; #7, isotropic contribution of the satellite transitions. δ_{iso} values are ± 0.15 ppm for #1–#3 and ± 0.08 ppm for #4–#6, C_Q values are ± 0.05 MHz, and η_Q values are ± 0.10 .

isotropic resonances, the contribution of the isotropic part of the satellite transitions was taken into account (see the Experimental Section and peak #7 in Figure 5). Five main peaks with an average intensity of ~18% (maximum 25%; minimum 12%) could be observed with significant variations of $C_Q(^{23}\text{Na})$. For three of the peaks (#4–#6 in Figure 5), the quadrupolar interaction was considered as negligible and Lorentz/Gauss line shapes were used for the simulations.

The crystal structure of $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (**1**), determined at 173 K by Anderson et al.,²⁰ exhibits only four distinct sodium sites in the asymmetric unit (see Table S2 in the Supporting Information). It follows that an apparent contradiction exists between expectations from the crystallography and the experimental number of isotropic ^{23}Na peaks observed at near room temperature (~318 K). One must remember that some disorder due to the presence of a unique $\text{NbO}_5\text{O}_{12}\text{H}$ site in the hexaniobate cluster must be considered to fully analyze the NMR spectra (see also Nb Echo MAS NMR). Such local disorder from one cluster to the other could explain the higher multiplicity of the ^{23}Na sites. Looking carefully at Figure 5, a sixth component (peak #3) could be extracted from the 2D 3QMAS experiment. The intensity of this particular peak derived from the 1D ^{23}Na spectrum is very small (~2%). We

make the reasonable assumption that this peak corresponds to an impurity. Indeed, even though special care was taken to remove the excess of NaOH necessary for the synthesis of **1**, we could not rule out that the appearance of the sixth sodium site in the MAS NMR spectrum of **1** resulted from the presence of a small proportion of fully deprotonated clusters $\text{Na}_8\text{Nb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$. This highlights the difficulty of isolating pure hexaniobate salts and the fact that multiple techniques are needed to discriminate between the numerous phases that can be formed (Table 1). No attempts were made to further assign the five major ^{23}Na resonances to particular Na sites in the structure of **1** or to correlate the variations of $C_Q(^{23}\text{Na})$ with the local chemical environment of sodium sites, as it would necessitate ab initio calculations of ^{23}Na parameters using supercells to take disorder into account.^{54,75} Such a work is outside the scope of this contribution.

In our attempt to further characterize polyoxometalates by NMR, we also probed $\text{Na}_8\text{Ta}_6\text{O}_{19} \cdot 24.5\text{H}_2\text{O}$ (**3**) by ^{23}Na MAS NMR. The spectrum of **3** recorded at 16.4 T and 30 kHz displayed a very complicated spectrum (Figure 6) which

Figure 6. ^{23}Na MAS NMR spectra of (solid line) $\text{Na}_8\text{Ta}_6\text{O}_{19} \cdot 24.5\text{H}_2\text{O}$ (**3**) and (dashed line) $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (**1**) for comparison. See Table S1 in the Supporting Information for NMR parameters.

involved most probably a superposition of Na sites with variable C_Q values. Importantly, the ^{23}Na chemical shifts observed for **3** were in the same range as for the hexaniobate salt **1**, indicating that $\text{Ta}_6\text{O}_{19}/\text{Nb}_6\text{O}_{19}$ clusters and water molecules have a similar effect on Na. The crystal structure of **3** was recently resolved by Abramov et al.¹⁷ and displays a layered structure with 10 nonequivalent sodium sites in the asymmetric unit. It follows that the analysis of the corresponding ^{23}Na MAS NMR spectrum should imply at least 10 nonequivalent contributions (if XRD data are strictly followed and no disorder is present). In order to further characterize **3**, a ^{23}Na 3Q MQ MAS experiment was performed (Figure S10 in the Supporting Information). Such an experiment led to a partial disentanglement of the corresponding ^{23}Na MAS spectrum. Indeed, two well-defined peaks were identified. The first peak is characterized by $\delta_{\text{iso}} = +0.50$ ppm and $C_Q = 1.80$ MHz (assuming here $\eta_Q = 1$). The second peak centered at $\delta_{\text{iso}} = +6.35$ ppm is not subject to any measurable quadrupolar interaction ($\text{LW} = 215$ Hz). Most interestingly, a much less defined component was evidenced as well. It remained difficult to characterize it more precisely due to the eventual presence of distributions of NMR parameters. In other words, X-ray diffraction data showing 10 nonequivalent sites (see above) could perhaps correspond to an average structure (exhibiting more structural complexity at the local NMR level).

Figure 7. ^{23}Na MAS NMR spectra of (black) $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) and (red) $\text{Na}_7\text{HfNb}_{5.67}\text{Ta}_{0.33}\text{O}_{19}\cdot 15\text{H}_2\text{O}$. The vertical red arrow stresses the differences between both spectra. Insert A: ^{93}Nb echo MAS NMR spectra of (black line) $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) and (red line) $\text{Na}_7\text{HfNb}_{5.67}\text{Ta}_{0.33}\text{O}_{19}\cdot 15\text{H}_2\text{O}$. Insert B: ^1H MAS NMR spectra of (black line) $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) and (red line) $\text{Na}_7\text{HfNb}_{5.67}\text{Ta}_{0.33}\text{O}_{19}\cdot 15\text{H}_2\text{O}$. See Table S1 in the Supporting Information for NMR parameters.

Study of Ta-Doped $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$. Finally, the Nb–Ta substitution in the cluster M_6O_{19} was investigated by solid-state MAS NMR. The synthesis of $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) was performed by alkaline fusion, as described in the Experimental Section, but Ta_2O_5 was added to the starting material (Nb_2O_5) before the synthesis. The Nb/Ta ratio used for the study was 17.4/1, which corresponds to the formula $\text{Na}_7\text{HfNb}_{5.67}\text{Ta}_{0.33}\text{O}_{19}\cdot 15\text{H}_2\text{O}$ or, in other words, one atom of tantalum for three M_6O_{19} clusters.

The substitution of niobium by tantalum in the cluster Nb_6O_{19} did not significantly influence the ^{93}Nb echo MAS NMR spectra (see insert A in Figure 7). Only a very slight smoothing of the discontinuities was observed. The lack of distinguishing the different sites is thought to be due to the intrinsic low resolution of ^{93}Na MAS NMR and most probably the low Ta doping rate used in the study. Moreover, the crystallographic structure of 1 is not expected to change significantly (as checked by powder XRD; data not shown), due to the low tantalum doping and due to the identical ionic radii of Ta(V) and Nb(V) (i.e., 64 pm if CN = 6). On the other hand, ^{23}Na MAS NMR was found to be more sensitive at following the Nb/Ta substitution in $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) (Figure 7). When 1 was doped with tantalum, the ^{23}Na MAS spectrum was clearly modified. The modification of the spectrum was further characterized by a ^{23}Na 3Q MAS experiment (Figure S11 in the Supporting Information). The importance of a peak at $\delta_{\text{iso}} = 4.75$ ppm, $C_Q = 2.31$ MHz, and $\eta_Q = 0.78$ was clearly evidenced. This corresponds to the main difference between 1 and the Ta-doped structure. The complete simulation of the ^{23}Na MAS spectrum (with relative integrations) is also given in Figure S11. A direct comparison can be established with data obtained for 1 (see Table 3). The complexity of the spectrum increases with Ta doping, in

agreement with the expected increase of structural disorder in the doped structure.

One realistic structural assumption is to suppose that the insertion of tantalum in $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) induced a partial substitution of the proton, linked to the cluster, by a sodium ion, leading to the general formula $\text{Na}_{7+y}\text{H}_{1-y}\text{Nb}_{5.67}\text{Ta}_{0.33}\text{O}_{19}\cdot 15\text{H}_2\text{O}$. Such an assumption was confirmed by ^1H solid-state MAS NMR. The insert B in Figure 7 gives a comparison between the ^1H NMR spectra of 1 and the Ta-doped sample. The broad peak at +6.3 ppm due to the water molecules and the much less intense peak at +1.9 ppm due to the $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ sites of the clusters in 1 were still observed, but an additional sharp peak appeared at $\sim +4.9$ ppm. This value is strictly comparable to those observed in Figure 3. As discussed for $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (2) and $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (3) (see H MAS NMR), the water molecules surrounding a fully deprotonated cluster exhibit a rather sharp (but composite) ^1H NMR resonance (see Figure 3). This means that, when the Nb/Ta substitutions took place, fully deprotonated clusters were formed, supporting the ^{23}Na NMR observations. A quantitative analysis of the loss of $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ sites upon substitution by Ta was not performed here, due to the complexity of the broad water resonance (see above).

The study of several deprotonated Nb_6O_{19} and Ta_6O_{19} structures, performed by Anderson et al.,²⁰ revealed that the Ta clusters have slightly longer M=O bonds in comparison to their Nb counterparts. For example, the average M=O distances in $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (1) and the isostructural $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (3) are 1.770 and 1.799 ± 0.003 Å, respectively. In the crystal of 1, the $\text{NbO}_5\text{O}_{\mu 2}\text{H}$ site has also the longest Nb=O bond length (1.780 vs 1.760 Å, respectively). Therefore, this site is more prone to accommodate the Nb–Ta substitution. This assumption was clearly

corroborated by ^1H MAS NMR data (insert B in Figure 7), where the resonance at ~ 4.9 ppm can be safely related to deprotonated clusters. Since **1** was synthesized by alkaline fusion at high temperature (450°C), Ta was initially expected to be homogeneously distributed.⁷⁶ However, as the ~ 4.9 ppm resonance is clearly observed in the ^1H MAS spectra, the following assumption can be proposed: the Ta atoms could be incorporated in *adjacent* clusters, leading to rather isolated groups of deprotonated entities surrounded by water molecules characterized by the rather sharp resonances at ~ 4.9 ppm. The example given here shows that the mixed-metal clusters can shed light on the differences between Nb and Ta chemistries. Moreover, one could take advantage of these differences and tune the physicochemical properties of hexametalate salts by preparing mixed Nb/Ta hexametalate salts. Obviously, multinuclear solid-state NMR appears to be a highly pertinent tool for providing accurate structural details on the mixed Nb/Ta clusters.

CONCLUSION AND PERSPECTIVES

This work highlights the potential of multinuclear MAS NMR techniques to study hexaniobate and hexatantalate salts. The studies of $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (**1**), $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ (**2**), and $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (**3**) showed that *protonated* and *deprotonated* clusters were easily discriminated by ^1H fast MAS and echo NMR. Moreover, we demonstrated that partial Nb/Ta substitution could be easily followed by ^1H MAS NMR, as the local dynamics of the water molecules at room temperature were shown to be strongly different between protonated and deprotonated clusters. Variable-temperature ^1H MAS NMR experiments will be performed in the near future in order to further investigate the local motion of the water molecules. ^{93}Nb echo MAS NMR spectra were recorded at ultrahigh field and ultrafast MAS (variable field and MAS frequency). It appeared that $\text{NbO}_5\text{O}_{1/2}\text{H}$ and NbO_6 were clearly distinguished on the basis of variations in $C_Q(^{93}\text{Nb})$ and relative intensities of the resonance lines. Cross polarization (CP) from ^1H to ^{93}Nb , as well as 2D ^1H – ^{93}Nb correlation experiments, could be interesting options to further characterize the protonated $\text{NbO}_5\text{O}_{1/2}\text{H}$ sites through spectral editing. Static ^{93}Nb spectra could be recorded (wide-line NMR spectroscopy)⁵⁵ under BRAIN (broadband adiabatic inversion pulses) CP transfer.⁷⁷ Such a sequence is indeed well adapted for CP dealing with “strong” quadrupolar nuclei (high $C_Q(^{93}\text{Nb})$ values). Work is currently in progress in our laboratory.

The ^{23}Na MAS and 3QMAS NMR study of **1** revealed several sodium sites and confirmed the presence of disorder due to the presence of a unique $\text{NbO}_5\text{O}_{1/2}\text{H}$ site per cluster. The high resolution observed in ^{23}Na MAS NMR should allow the setup of 2D homonuclear dipolar (^{23}Na – ^{23}Na) experiments in order to correlate the ^{23}Na nuclei.⁷⁸ This approach could be of great interest for accurate analysis in the case of mixtures of hexaniobate/tantalate clusters, as ^{23}Na NMR is sensitive to the chemical nature of the clusters. Very interestingly, the Nb/Ta substitution in **1** was found to be easier to follow by ^{23}Na and ^1H MAS NMR than by ^{93}Nb MAS NMR due to the exchange between the protons linked to the cluster and sodium ion. Finally, we mention that ^{181}Ta ($I = 7/2$) could be another local probe of investigation, but it can be considered to be a “very strong” quadrupolar nucleus.⁷⁹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00345.

SEM images, Raman spectra, and TGA analyses of **1**–**3**, ^{93}Nb static WURST QCPMG spectra of NaNbO_3 and **1**, ^{23}Na 3Q MAS spectra of **2** and **3**, summary of NMR parameters used in this study, and crystal structure information for **1**–**3** (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail for G.J.-P.D.: gauthier.deblonde@chimie-paris.org.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. Marie-Noëlle Rager (Chimie ParisTech) for helpful discussions. This work was supported by Eramet Research (France). The French Région Ile de France SESAME program is acknowledged for financial support (700 MHz spectrometer). The UK 850 MHz solid-state NMR facility used in this research was funded by the EPSRC and BBSRC as well as the University of Warwick, including via partial funding through Birmingham Science City Advanced Materials Projects 1 and 2 supported by Advantage West Midlands (AWM) and the European Regional Development Fund (ERDF).

REFERENCES

- (1) *The economics of niobium*; Roskill Information Services: London, 2009.
- (2) Nete, M.; Purcell, W.; Nel, J. T. *Hydrometallurgy* **2014**, *149*, 31–40.
- (3) Agulyanski, A. *The chemistry of tantalum and niobium fluoride compounds*, 1st ed.; Elsevier: Amsterdam and Boston, 2004.
- (4) Deblonde, G. J.-P.; Chagnes, A.; Weigel, V.; Cote, G. *Hydrometallurgy* **2016**, DOI: 10.1016/j.hydromet.2015.12.009.
- (5) Deblonde, G. J.-P.; Weigel, V.; Bellier, Q.; Houdard, R.; Delvallée, F.; Bélair, S.; Beltrami, D. *Sep. Purif. Technol.* **2016**, *162*, 180–187.
- (6) Wang, X.; Zheng, S.; Xu, H.; Zhang, Y. *Hydrometallurgy* **2009**, *98*, 219–223.
- (7) Marignac, M. C. *Ann. Chim. Phys.* **1866**, *8*, 5–75.
- (8) Nyman, M. *Dalton Trans.* **2011**, *40*, 8049–8058.
- (9) Deblonde, G. J.-P.; Moncomble, A.; Cote, G.; Bélair, S.; Chagnes, A. *RSC Adv.* **2015**, *5*, 7619–7627.
- (10) Deblonde, G. J.-P.; Delaunay, N.; Lee, D.; Chagnes, A.; Cote, G. *RSC Adv.* **2015**, *5*, 64119–64124.
- (11) Lindqvist, I. *Ark. Kemi* **1953**, *5*, 247–250.
- (12) Zhou, H.; Zheng, S.; Zhang, Y. *Hydrometallurgy* **2005**, *80*, 83–89.
- (13) Zhou, H.; Zheng, S.; Zhang, Y.; Yi, D. *Hydrometallurgy* **2005**, *80*, 170–178.
- (14) Nyman, M.; Anderson, T. M.; Provencio, P. P. *Cryst. Growth Des.* **2009**, *9*, 1036–1040.
- (15) Shen, L.; Xu, Y.-Q.; Gao, Y.-Z.; Cui, F.-Y.; Hu, C.-W. *J. Mol. Struct.* **2009**, *934*, 37–43.
- (16) Britvin, S. N.; Siidra, O. I.; Lotnyk, A.; Kienle, L.; Krivovichev, S. V.; Depmeier, W. *Inorg. Chem. Commun.* **2012**, *25*, 18–20.
- (17) Abramov, P. A.; Abramova, A. M.; Peresypkina, E. V.; Gushchin, A. L.; Adonin, S. A.; Sokolov, M. N. *J. Struct. Chem.* **2011**, *52*, 1012–1017.
- (18) Deblonde, G. J.-P.; Chagnes, A.; Bélair, S.; Cote, G. *Hydrometallurgy* **2015**, *156*, 99–106.

- (19) Muller, M. *Rev. Chim. Minérale* **1970**, *7*, 359.
- (20) Anderson, T. M.; Rodriguez, M. A.; Bonhomme, F.; Bixler, J. N.; Alam, T. M.; Nyman, M. *Dalton Trans.* **2007**, *40*, 4517–4522.
- (21) Pickhard, F.; Hartl, H. Z. *Anorg. Allg. Chem.* **1997**, *623*, 1311–1316.
- (22) Balogh, E.; Anderson, T. M.; Rustad, J. R.; Nyman, M.; Casey, W. H. *Inorg. Chem.* **2007**, *46*, 7032–7039.
- (23) Sahureka, F.; Burns, R. C.; von Nagy-Felsobuki, E. I. *Inorg. Chim. Acta* **2003**, *351*, 69–78.
- (24) Matsumoto, M.; Ozawa, Y.; Yagasaki, A. *Inorg. Chem. Commun.* **2011**, *14*, 115–117.
- (25) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93–103.
- (26) Besserguenev, A. V.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2001**, *40*, 2582–2586.
- (27) Nelson, H. W.; Tobias, S. *Inorg. Chem.* **1963**, *2*, 985–992.
- (28) Farrell, F. J.; Maroni, V. A.; Spiro, T. G. *Inorg. Chem.* **1969**, *8*, 2638–2642.
- (29) Aveston, J.; Johnson, J. S. *Inorg. Chem.* **1964**, *3*, 1051–1053.
- (30) Dehand, J. *Rev. Chim. Minérale* **1965**, *2*, 259–293.
- (31) Hartl, H.; Pickhard, F.; Emmerling, F.; Röhr, C. Z. *Anorg. Allg. Chem.* **2001**, *627*, 2630–2638.
- (32) Matsumoto, M.; Ozawa, Y.; Yagasaki, A. *Inorg. Chem.* **2012**, *51*, 5991–5993.
- (33) Matsumoto, M.; Ozawa, Y.; Yagasaki, A.; Zhe, Y. *Inorg. Chem.* **2013**, *52*, 7825–7827.
- (34) Hou, Y.; Fast, D. B.; Ruther, R. E.; Amador, J. M.; Fullmer, L. B.; Decker, S. R.; Zakharov, L. N.; Dolgos, M. R.; Nyman, M. *J. Solid State Chem.* **2015**, *221*, 418–425.
- (35) Flynn, C. M., Jr; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 332–334.
- (36) Alam, T. M.; Nyman, M.; Cherry, B. R.; Segall, J. M.; Lybarger, L. E. *J. Am. Chem. Soc.* **2004**, *126*, 5610–5620.
- (37) Tong, H.; Ye, J. *Eur. J. Inorg. Chem.* **2010**, *2010*, 1473–1480.
- (38) Niu, J.; Ma, P.; Niu, H.; Li, J.; Zhao, J.; Song, Y.; Wang, J. *Chem. - Eur. J.* **2007**, *13*, 8739–8748.
- (39) Bonhomme, F.; Larentzos, J. P.; Alam, T. M.; Maginn, E. J.; Nyman, M. *Inorg. Chem.* **2005**, *44*, 1774–1785.
- (40) Goiffon, A.; Philippot, E.; Maurin, E. *Rev. Chim. Minérale* **1980**, *17*, 466–476.
- (41) Nyman, M.; Celestian, A. J.; Parise, J. B.; Holland, G. P.; Alam, T. M. *Inorg. Chem.* **2006**, *45*, 1043–1052.
- (42) Kinomura, N.; Kumata, N.; Muto, F. *Mater. Res. Bull.* **1984**, *19*, 299–304.
- (43) Kennedy, J. H. *J. Inorg. Nucl. Chem.* **1961**, *20*, 53–57.
- (44) Zhang, D.; Li, S.; Wang, J.; Niu, J. *Inorg. Chem. Commun.* **2012**, *17*, 75–78.
- (45) Ma, P.; Wang, G.; Chen, G.; Wang, J.; Niu, J. *J. Mol. Struct.* **2011**, *997*, 126–130.
- (46) Nyman, M.; Alam, T. M.; Bonhomme, F.; Rodriguez, M. A.; Frazer, C. S.; Welk, M. E. *J. Cluster Sci.* **2006**, *17*, 197–219.
- (47) Black, J. R.; Nyman, M.; Casey, W. H. *J. Am. Chem. Soc.* **2006**, *128*, 14712–14720.
- (48) Neumann, G. *Acta Chem. Scand.* **1964**, *18*, 278–280.
- (49) Kong, X.; Hu, D.; Wen, P.; Ishii, T.; Tanaka, Y.; Feng, Q. *Dalton Trans.* **2013**, *42*, 7699–7709.
- (50) Santos, I.; Loureiro, L. H.; Silva, M. F. P.; Cavaleiro, A. *Polyhedron* **2002**, *21*, 2009–2015.
- (51) Ohlin, C. A.; Villa, E. M.; Fetting, J. C.; Casey, W. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 8251–8254.
- (52) Ohlin, C. A.; Villa, E. M.; Casey, W. H. *Inorg. Chim. Acta* **2009**, *362*, 1391–1392.
- (53) Maekawa, M.; Ozawa, Y.; Yagasaki, A. *Inorg. Chem.* **2006**, *45*, 9608–9609.
- (54) Papulovskiy, E.; Shubin, A. A.; Terskikh, V. V.; Pickard, C. J.; Lapina, O. B. *Phys. Chem. Chem. Phys.* **2013**, *15*, 5115–5131.
- (55) Hanna, J. V.; Pike, K. J.; Charpentier, T.; Kemp, T. F.; Smith, M. E.; Lucier, B. E. G.; Schurko, R. W.; Cahill, L. S. *Chem. - Eur. J.* **2010**, *16*, 3222–3239.
- (56) Zhou, D. H.; Hoatson, G. L.; Vold, R. L. *J. Magn. Reson.* **2004**, *167*, 242–252.
- (57) Schurko, R. W. *Acc. Chem. Res.* **2013**, *46*, 1985–1995.
- (58) Iuga, D.; Schäfer, H.; Verhagen, R.; Kentgens, A. P. J. *Magn. Reson.* **2000**, *147*, 192–209.
- (59) Medek, A.; Harwood, J. S.; Frydman, L. *J. Am. Chem. Soc.* **1995**, *117*, 12779–12787.
- (60) Amoureux, J.-P.; Fernandez, C.; Steuernagel, S. *J. Magn. Reson., Ser. A* **1996**, *123*, 116–118.
- (61) Sakellariou, D.; Lesage, A.; Hodgkinson, P.; Emsley, L. *Chem. Phys. Lett.* **2000**, *319*, 253–260.
- (62) Massiot, D. *Quadrupolar + CSA Static and MASldmfit; NMR@CEMHTI, CNRS UPR3079, Orléans, France; http://nmr.cemhti.cnrs-orleans.fr/dmfit/help/models/QUAD_CSA.aspx* (accessed Feb 9, 2016).
- (63) Grey, C. P.; Vega, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8232–8242.
- (64) Pourpoint, F.; Gervais, C.; Bonhomme-Courty, L.; Azaïs, T.; Coelho, C.; Mauri, F.; Alonso, B.; Babonneau, F.; Bonhomme, C. *Appl. Magn. Reson.* **2007**, *32*, 435–457.
- (65) Alam, T. M.; Nyman, M.; McIntyre, S. K. *J. Phys. Chem. A* **2007**, *111*, 1792–1799.
- (66) Jehng, J.-M.; Wachs, I. E. *Chem. Mater.* **1991**, *3*, 100–107.
- (67) Johnston, K. E.; Griffin, J. M.; Walton, R. L.; Dawson, D. M.; Lightfoot, P.; Ashbrook, S. E. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7565–7576.
- (68) Yamada, K.; Shimizu, T.; Nakai, T.; Deguchi, K.; Yue, B.; Ye, J. *Chem. Lett.* **2013**, *42*, 1223–1224.
- (69) Chenu, S.; Werner-Zwanziger, U.; Calahoo, C.; Zwanziger, J. W. *J. Non-Cryst. Solids* **2012**, *358*, 1795–1805.
- (70) Papulovskiy, E.; Khabibulin, D. F.; Terskikh, V. V.; Paukshtis, E. A.; Bondareva, V. M.; Shubin, A. A.; Andreev, A. S.; Lapina, O. J. *Phys. Chem. C* **2015**, *119*, 10400–10411.
- (71) Perić, B.; Gautier, R.; Pickard, C. J.; Bosiočić, M.; Grbić, M. S.; Požek, M. *Solid State Nucl. Magn. Reson.* **2014**, *59–60*, 20–30.
- (72) Ghose, S.; Tsang, T. *Am. Mineral.* **1973**, *58*, 748–755.
- (73) MacKenzie, K. J. D.; Smith, M. E. *Multinuclear Solid-State Nuclear Magnetic Resonance of Inorganic Materials*; Elsevier Science: Amsterdam, 2002; Pergamon Materials Series Vol. 6.
- (74) Skibsted, J.; Brorson, M.; Villadsen, J.; Jakobsen, H. J. *Inorg. Chem.* **2000**, *39*, 4130–4136.
- (75) Bonhomme, C.; Gervais, C.; Babonneau, F.; Coelho, C.; Pourpoint, F.; Azaïs, T.; Ashbrook, S. E.; Griffin, J. M.; Yates, J.; Mauri, F.; Pickard, C. J. *Chem. Rev.* **2012**, *112*, 5733–5779.
- (76) Deblonde, G. J.-P.; Chagnès, A.; Cote, G.; Vial, J.; Rivals, I.; Delaunay, N. *J. Chromatogr. A* **2016**, *1437*, 210–218.
- (77) Harris, K. J.; Lupulescu, A.; Lucier, B. E. G.; Frydman, L.; Schurko, R. W. *J. Magn. Reson.* **2012**, *224*, 38–47.
- (78) Eden, M.; Frydman, L. *J. Phys. Chem. B* **2003**, *107*, 14598–14611.
- (79) Rod, S.; Borsa, F.; Van der Klink, J. J. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *38*, 2267–2272.