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The First Observation of Heteronuclear Two-Bond *J*-Coupling in the Solid State: Crystal Structure and Solid-State NMR Spectroscopy of $Rb_4(NbO)_2(Si_8O_{21})$

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High-temperature, high-pressure hydrothermal synthesis of the title compound and its ^{93}Nb and ^{29}Si MAS NMR spectra are reported. The ^{29}Si MAS NMR spectrum shows four signals corresponding to the four distinct Si sites in the structure. Three signals show multiplet patterns which arise from ^{93}Nb(spin-$^9/_2$)–^{29}Si *J*-coupling. This is the first example of two-bond *J*-coupling between a quadrupolar nucleus and a spin-$^1/_2$ nucleus in the solid state. A combination of ^{93}Nb and ^{29}Si solid-state NMR and X-ray diffraction data has provided a correlation between NMR interaction parameters and local structure. This work opens a new opportunity to examine the relationship between ^2J-coupling and structural parameters in the solid state.

Indirect spin–spin coupling constants (*J*-coupling) between nuclei provide an important NMR parameter that contains not only information about chemical connectivity but also geometrical information as first shown by Karplus in 1959.[1] However, observations of indirect spin–spin coupling between spin-$^1/_2$ and quadrupolar nuclei in solution NMR studies are often hampered, owing to the rapid, quadrupole-dominated spin–lattice relaxation of the quadrupolar nucleus. It is, on the other hand, possible to measure *J*-couplings from the spin-$^1/_2$ spectra if the coupled quadrupolar nucleus exists within a symmetric environment, which results in reduced values of the quadrupolar coupling constant (C_Q) and longer spin–lattice relaxation times for the quadrupolar nucleus. The effects of spin–spin coupling between spin-$^1/_2$ (I) and quadrupolar nuclei (S) on the solid-state NMR spectrum of the spin-$^1/_2$ nucleus are well-documented, and measurements of one-bond *J*-couplings on a wide variety of spin pairs have been made.[2,3] Here we report signal splitting patterns of the ^{29}Si NMR signals, due to $^2J(^{93}\mathrm{Nb},^{29}\mathrm{Si})$ coupling, of a niobium silicate, $Rb_4(NbO)_2(Si_8O_{21})$, denoted as **1**. To the best of our knowledge, this provides the first example of two-bond *J*-coupling between a quadrupolar nucleus and a spin-$^1/_2$ nucleus in the solid state.

Compound **1** was obtained from a high-temperature, high-pressure hydrothermal reaction in a gold ampule contained in a Leco Tem-Pres autoclave where pressure was provided by water. The degree of filling of the autoclave by water at room temperature is 55%. A reaction mixture of 0.3 mL of $RbOH_{aq}$ (50 wt %), 0.1063 g of Nb_2O_5, and 0.2043 g of SiO_2 (molar ratio Rb:Nb:Si = 3:0.94:4) in a 4.3 cm long gold ampule (inside diameter = 4.85 mm) was heated at 500 °C for 3 days. The pressure was estimated to be 110 MPa. The autoclave was then cooled to 300 °C at 5 °C/h and quenched at room temperature by removing the autoclave from the furnace. The product contained colorless rod crystals and powder. EDX analysis of several crystals showed the presence of Rb, Si, and Nb. A colorless rod crystal was selected for single-crystal X-ray diffraction study.[4] A single-phase product of **1** was obtained as indicated by powder X-ray diffraction of the bulk product. The yield was 82% based on niobium. The sample was used for solid-state NMR study.

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(1) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.

(2) Harris, R. K.; Oliveri, A. C. *Prog. NMR Spectrosc.* **1992**, *24*, 435.

(3) Some examples include the following: (a) Andrew, E. R.; Farnell, L. F.; Gledhill, T. D. *Phys. Rev. Lett.* **1967**, *19*, 6. (b) Andrew, E. R.; Firth, M.; Jasinski, A.; Randall, P. *J. Phys. Lett.* **1970**, *31A*, 446. (c) Olivieri, A. C. *Magn. Reson. Chem.* **1996**, *34*, 365. (d) Christendat, D.; Markwell, R. D.; Gilson, D. F. R.; Butler, I. S.; Cotton, J. D. *Inorg. Chem.* **1997**, *36*, 230. (e) Heise, H.; Kohler, F. H.; Brouwer, E. B.; Harris, R. K.; Steuernagel, S. *Magn. Reson. Chem.* **1999**, *37*, 573.

(4) Crystal data for **1**: $Nb_2O_{23}Rb_4Si_8$, colorless crystal of dimensions $0.25 \times 0.10 \times 0.05$ mm, $T = 294$ K, triclinic; space group $P\bar{1}$ (No. 2); $a = 6.8977(5)$ Å, $b = 7.7585(5)$ Å, $c = 11.0133(7)$ Å, $\alpha = 76.490(1)°$, $\beta = 89.287(1)°$, $\gamma = 71.831(1)°$, $V = 543.3(1)$ Å^3; $Z = 1$; $\rho_{calcd} = 3.424$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 105.1$ cm^{-1}, 2225 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.5°$, R(int) = 0.0327), GOF = 1.060, R1 = 0.0209, wR2 = 0.0562. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all atoms. Diffractometer: Siemens Smart CCD (Mo Kα radiation, graphite monochromator). Structure solution and refinement: SHELXTL (Sheldrick, G. M. Version 5.1, Siemens Analytical X-ray Instruments, Madison, WI, 1998). Absorption correction: SADABS (Sheldrick, G. M., University of Göttingen, 1995).

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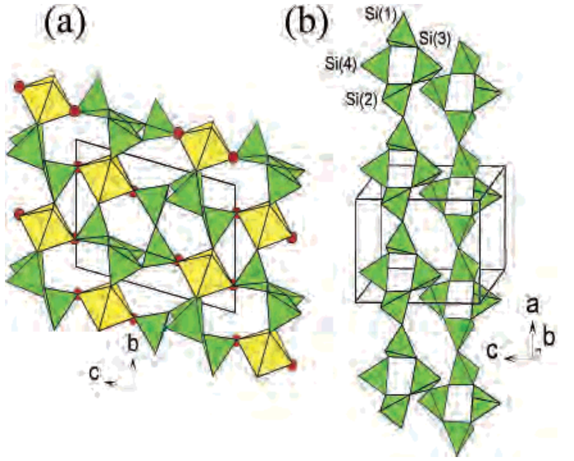

Figure 1. (a) Structure of **1** viewed along the *a* axis. The yellow and green polyhedra are NbO_6 octahedra and SiO_4 tetrahedra, respectively. Red circles are rubidium atoms. (b) Section of a double string of Si_4O_{12} rings in **1**.

Compound **1** is isotypic to $Cs_4(NbO)_2(Si_8O_{21})$, which was prepared by solid-state reaction at 1100 °C.[5] Its structure consists of infinite ribbons of corner-sharing SiO_4 tetrahedra running along the *a* axis and linked together via corner-sharing by NbO_6 octahedra to form a 3-D framework which delimits channel-like cavities to accommodate Rb^+ cations (Figure 1a). Each ribbon is formed of double strings of Si_4O_{12} rings. Each ring is connected to two rings within a string and one ring in the adjacent string (Figure 1b).

The NbO_6 octahedron shares five of its corners with three different ribbons with its sixth corner being unshared. The silicate groups are nearly regular with the Si−O bond distances ranging from 1.570 to 1.635 Å. The shortest distance in each silicate group corresponds to the oxygen atom bonded to niobium. $Si(1)O_4$, $Si(2)O_4$, and $Si(3)O_4$ each shares corners with three silicate groups and one NbO_6 octahedron, while $Si(4)O_4$ shares corners with two silicate groups and two NbO_6 octahedra. The Si−O−Nb bond angles are in the range from 136.3° to 141.3° for Si(1), Si(2), and Si(4). In contrast, the Si(3)−O−Nb bond angle is nearly linear (173.8°). In NbO_6 the oxygen atom that is not shared with any silicate group is most tightly bonded to the central atom, as evidenced by the shortest Nb═O bond length of 1.746 Å. The bond to the oxygen atom in the trans position is the longest (2.195 Å). The other four Nb−O bond lengths are in the range from 1.984 to 2.043 Å.

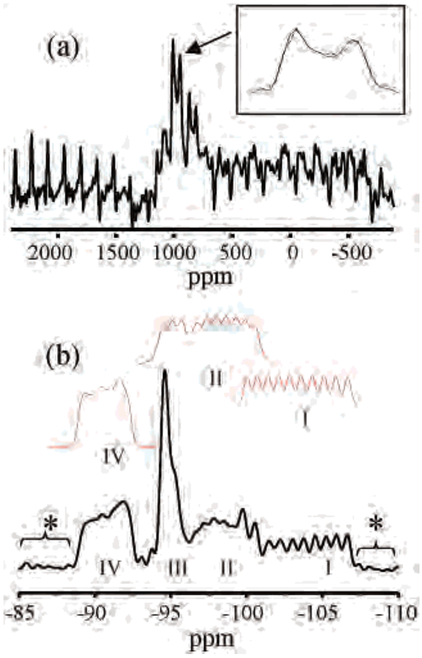

Figure 2. (a) ^{93}Nb MAS NMR spectrum of **1** obtained at room temperature and at a spinning speed of 12 kHz. Simulation of central band is shown in dashed line in the inset. (b) ^{29}Si MAS NMR spectrum of **1** obtained at room temperature and at a spinning speed of 5 kHz. Four silicon sites were observed as labeled. Simulated spectra (in red) of sites I, II, and IV were made by the NMR parameters listed in Table 1. Asterisks denote spinning sidebands.

The ^{93}Nb MAS (magic angle spinning) NMR spectrum is shown in Figure 2a.[6] The spinning sidebands are well separated from the central transition in the spectrum, permitting analysis of the isotropic central band. Simulations of the isotropic central band, as shown in dashed lines in the inset, yield values of C_Q, η, and δ_{iso} equal to 20.5(5) MHz, 0.15(5), and 1042(10) ppm, respectively (estimated errors are in parentheses). The value of $C_Q(^{93}Nb)$ for **1** is close to those for $NaNbO_3$ and $LiNbO_3$ (19.5 and 22 MHz, respectively).[7,8]

Figure 2b shows the ^{29}Si MAS NMR spectrum of **1**. Four signals are observed as labeled, consistent with four distinct silicon sites as determined from X-ray diffraction. Surprisingly, three of them show multiplet patterns, which arise from two-bond $^{93}Nb(\text{spin-}^{9}/_{2})-^{29}Si$ *J*-coupling. There have been no reports on $J(^{93}Nb,^{29}Si)$ measured in the solid state. However, $^1J(^{93}Nb,^{19}F)$ and $^1J(^{93}Nb,^{31}P)$ have been measured in solid K_2NbF_7 and the niobium half-sandwich complex via ^{19}F and ^{31}P MAS NMR experiments, respectively.[9,10] The multiplet pattern of site I is much better resolved as compared to the other sites. The 10 peaks of site I are not evenly spaced in that the spacing between adjacent peaks decreases slightly with decreasing frequency, and two of them overlap with site II. The very different spectral feature of site III can be attributed to Si(4) because it is connected to two NbO_6 octahedra.

For the present case where $(C_Q/4S(2S-1)\nu_S) \ll 1$, the frequency shifts of the $2S+1$ peaks away from the isotropic

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(6) The ^{93}Nb MAS spectra were obtained using a Hahn-echo sequence. ^{93}Nb MAS spectra were collected at 9.4 T using a 4 mm probe with rf fields of 100 kHz, with effective 90° pulse widths of 0.4 μs measured on actual solid samples ($\pi/12$ when measured with the solution standard) and pulse delays of 0.5 s. The ^{29}Si MAS NMR spectrum was acquired with a 45° pulse width of 3.0 μs and a repetition time of 20 s. ^{93}Nb and ^{29}Si chemical shifts were referenced with respect to 1 M $Nb(NO_3)_{5aq}$ and TMS, respectively.

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(10) Gibson, V. C.; Gobetto, R.; Harris, R. K.; Langdale-Brown, C.; Siemeling, U. *J. Organomet. Chem.* **1994**, *479*, 207.

chemical shift of the nucleus can be calculated by a first-order perturbation treatment:[2]

$$\Delta\nu_m = -mJ + \left(\frac{3D'C_Q}{20\nu_S}\right)\left[\frac{S(S+1)-3m^2}{S(2S-1)}\right](3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2\alpha^D) \tag{1}$$

where m is the magnetic quantum number of nucleus S, J is the isotropic $I{-}S$ indirect coupling constant, ν_S is the resonance frequency of the quadrupolar nucleus, β^D and α^D are the angles that describe the orientation of the dipolar vector with respect to the EFG tensor, D' is the effective dipolar coupling constant, given by $D' = D - \Delta J/3$ by assuming that the **J**-tensors are collinear with the internuclear vector r_{I-S}, where D is the dipolar coupling constant that can be calculated from the crystallographically derived Nb−Si distances (in a range from 3.4 to 3.6 Å), and ΔJ is the anisotropy in the **J**-tensor, which is small compared to D and does not have any observable effects on the ^{29}Si NMR spectra.

An isotropic J-coupling of 64 Hz for site I can be determined from the spacings between the central peaks of the multiplet pattern, which result from coupling to the $+^1/_2$ and $-^1/_2$ spin states of the niobium nucleus. An accurate measurement of J-coupling for sites II and IV appears to be difficult because the peaks are not well resolved. Since ^{93}Nb MAS NMR results indicate that the ^{93}Nb EFG tensor is nearly axially symmetric, it is reasonable to assume that the largest component of the EFG is located along the Nb═O bond, and thus the azimuthal angle (β^D) between internuclear vector and the EFG tensor can be determined. These parameters combined with the quadrupolar and dipolar coupling constants obtained from ^{93}Nb MAS NMR and X-ray structure, respectively, were used as initial values to simulate the experimental ^{29}Si NMR spectrum, and other parameters were varied until an acceptable fit was obtained. The spinning sidebands of the experimental spectra were summed prior to comparison of experimental and calculated results. Experimental and simulated spectra for these three Si sites are compared in Figure 2b. The parameters used in the simulations are summarized in Table 1. It is interesting to note that the Si(3) site with the largest Si−O−Nb angle exhibits the smallest J-coupling value and the most downfield shift, contrary to the trend of shifts predicted by the empirical relationship with Si−O−T bond angles for silicates.[11] Our measured values of $^2J(^{93}\text{Nb},^{29}\text{Si})$ for **1** are comparable to the value of $^2J(^{93}\text{Nb},^{19}\text{F})$ for $[\text{Nb(PF}_3)_6]^-$ (55 Hz) which was obtained from solution NMR.[12] This work reports the first direct measurement of heteronuclear two-bond J-coupling in the solid state. The ^2J-coupling between two nuclei depends on a variety of factors including the coordination number, bond angle, and formal hybridization of coupled nuclei. Further studies on several other niobium silicates are in progress in order to correlate the measured J-coupling with structural parameters.

Table 1. Best-Fit NMR Parameters and Assignments for ^{93}Nb−^{29}Si Spin Pairs in **1**

site	δ_{iso} (ppm)	D' (Hz)[a]	$\lvert ^2J \rvert$ (Hz)[b]	α^D, β^D (deg)[c]	assignment	∠Si−O−Nb (deg)[d]
I	−103.5	−136.3	64.0	80, 160	Si(1)	138.6
II	−97.9	−149.2	41.5	45, 110	Si(2)	136.3
IV	−91.0	−129.4	35.0	90, 95	Si(3)	173.8

[a] Estimated D' values were calculated from crystallographically derived Nb−Si bond distances by assuming that $\Delta J/3$ is negligible. Negative D' values are due to the negative gyromagnetic value of the ^{29}Si nucleus. [b,c] Estimated errors are ±0.5 Hz and ±10°, respectively. [d] Determined from X-ray diffraction.

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Supporting Information Available: Crystallographic data for $\text{Rb}_4(\text{NbO})_2(\text{Si}_8\text{O}_{21})$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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