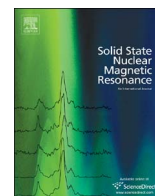




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Multinuclear solid-state magnetic resonance study of oxo-bridged diniobium and quadruply-bonded dimolybdenum carboxylate clusters[☆]

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ABSTRACT

Carboxylate paddlewheels and their oxo-bridged analogues constitute ideal building blocks for the assembly of two- and three-dimensional framework materials. Here, we present a multinuclear (¹H, ¹³C, ⁹³Nb, ⁹⁵Mo) magnetic resonance study of solid samples of Nb₂OCl₆(O₂Ph)₂ (**1**), Mo₂(O₂CMe)₄ (**2**), and Mo₂(O₂CCHF₂)₄ (**3**). High-resolution proton and ¹³C CP/MAS NMR spectra provide valuable information on structure and crystal symmetry and on cocrystallized solvent. ⁹³Nb solid-state NMR spectra of **1** provide quadrupolar coupling constants and chemical shift tensors which are characteristic of the axially asymmetric Nb-O-Nb bridging environment. ⁹⁵Mo solid-state NMR spectra of **2** and **3** provide quadrupolar coupling constants and chemical shift tensors which are directly characteristic of the molybdenum-molybdenum quadruple bonds in these compounds. The quadruple bonds are characterized by particularly large ⁹⁵Mo chemical shift tensor spans on the order of 5500 ppm. Density functional theoretical computations provide good agreement with the ⁹³Nb and ⁹⁵Mo experimental data, with some exceptions noted. This work demonstrates possible NMR approaches to characterize more complex framework materials and provides key insight into the Mo-Mo quadruple bond.

1. Introduction

The nature of bonding between metal ions in discrete clusters is a topic of great fundamental and applied interest [1]. The synthesis and subsequent detailed structural characterization of the [Re₂Cl₈]²⁻ dianion by Cotton in 1965, and their rationalization of the incredibly short Re...Re distance (2.242 Å) as a result of the presence of a quadruple bond, is a landmark achievement in contemporary inorganic chemistry [2]. The rapid acceleration in the discovery of metal-metal (M-M) bonded systems (single, double, triple, quadruple, and quintuple M-M bonded systems are all known) has provided an opportunity for the use of experimentation in developing the theoretical understanding of the nature of M-M bonded systems using solid-state NMR (SSNMR) spectroscopy. Selected examples to date include ^{185/187}Re SSNMR studies of the rhenium-rhenium bond in Re₂(CO)₁₀, [3] ⁷¹Ga SSNMR studies of the nature of the gallium-gallium bonds in a series of compounds including gallanes, gallenes, and gallynes, [4,5] ⁵⁵Mn SSNMR studies of the manganese-manganese bond in Mn₂(CO)₁₀, [6] and ¹¹B SSNMR analyses of multiple bonding in boron compounds [6–8]. Depending on the relative magnitudes of the quadrupolar coupling, chemical shift, and indirect nuclear spin-spin (*J*)

coupling interactions, valuable insights into the nature of the bonding between metals (or metalloids in the case of boron) were obtained.

A particularly well-known family of M-M bonded systems are the so-called paddlewheel carboxylates, of the type [M₂X₄] (M=Nb, Cr, Mo, Ta, W, Re, Ru, Os, Rh, and Ir are known), which feature M-M bonds of varying bond order (depending on the metal) surrounded by a tetracarboxylate ligand field [1]. With carboxylate ligand substitution typically facile and high-yielding, carboxylate paddlewheels and their oxo-bridged analogues constitute ideal building blocks for the assembly of two- and three-dimensional framework materials [9–12]. Here, we present a multinuclear (¹H, ¹³C, ⁹³Nb, ⁹⁵Mo) magnetic resonance study of solid samples of Nb₂OCl₆(O₂Ph)₂ (**1**), Mo₂(O₂CMe)₄ (**2**), and Mo₂(O₂CCHF₂)₄ (**3**). The niobium compound features two crystallographically distinct Nb ions which are bridged by an intervening oxygen atom. The molybdenum paddlewheels feature quadruply-bonded molybdenum spin pairs [1]. The structures of the symmetric bimetallic carboxylate clusters (**1** and **2**) were previously probed using X-ray diffraction [13,14]. The crystal structure for the difluoroacetate analogue **3** remains unknown; however, some studies of its structure in solution have been reported [15].

As is well-known to the readers of this journal, high-field SSNMR is

[☆] In honor of the exceptional contributions of J.-P. Amoureux to solid-state NMR spectroscopy. SI: Quadrupolar nuclei.

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powerful tool for the analysis of NMR-active nuclei with large quadrupole moments (Q), with low gyromagnetic ratios (γ), with low natural abundance (N.A.), or combinations of these attributes [16]. ^{93}Nb is a spin-9/2 nuclide with $Q=-320$ mb, $\gamma=6.5674\times 10^7$ rad T^{-1} s^{-1} , and a N.A. of 100% [17,18]. ^{95}Mo (spin 5/2) has a much smaller quadrupole moment but is less receptive overall ($Q=-22$ mb, $\gamma=-1.751\times 10^7$ rad T^{-1} s^{-1} ; N.A. of 15.92%) [17,18].

Recent ^{93}Nb SSNMR spectroscopy studies have focussed on a range of systems including sodium-niobium phosphate glasses, [19] half-sandwich niobium(I) and niobium(V) cyclopentadienyl complexes, [20] and various inorganic niobates [21–25]. Such studies have provided a wealth of pertinent structural information using advanced one- and two-dimensional SSNMR techniques (QCPMG and MQ/MAS, ST/MAS, etc.). Lapina and co-workers have provided a thorough overview of the ^{93}Nb SSNMR literature as well as various practical aspects of the experiments [26]. A useful ^{93}Nb chemical shift scale for NbO_x polyhedra, depending on the coordination number x and ranging from -500 to -2000 ppm, has been provided as well [27]. The value of computational chemistry, in particular density functional theoretical (DFT) methods, in understanding the niobium NMR parameters and their relationship to structure has been highlighted in the literature [20,22–24,28]. In particular, various relationships between NMR parameters and coordination number in a large series of niobates have been explored [24].

Similarly, the combination of high magnetic fields and sophisticated pulse techniques has continued to enable the structural study of various molybdenum systems using ^{95}Mo SSNMR spectroscopy. For example, following early work on catalysts, [29,30] recent detailed studies have been reported for crystalline and glassy inorganic molybdates, [31–36] a molybdenum piano stool complex, [37] and molybdenum carbonyl and phosphine complexes.[32] DFT studies are also expected to play an important role in the analysis and understanding of ^{95}Mo NMR parameters [38].

2. Experimental methods

2.1. Sample preparation

The syntheses of $[\text{Nb}_2\text{OCl}_6(\text{O}_2\text{Ph})_2]$ [13] (**1**), $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ [39] (**2**) and $[\text{Mo}_2(\text{O}_2\text{CHF}_2)_4]$ [40] (**3**) were adapted from literature procedures. Unless otherwise specified, all manipulations were performed under argon gas using standard Schlenk line or glovebox techniques. All glassware was oven dried (120°C , 6 h) and cooled under vacuum prior to use. Dichloromethane, diethyl ether, and acetonitrile were dried using a commercial solvent purification system designed by JC Meyer Solvent Systems and stored over 4 Å molecular sieves. Chloroform was dried using activated alumina and stored over 4 Å molecular sieves. All chemicals were purchased from commercial sources (Sigma Aldrich, Strem Chemical) and used without further purification, with the exception of benzoic acid which was recrystallized from petroleum ether and dried *in vacuo* for several hours prior to use. The unit cells of single crystals obtained from the syntheses were examined via X-ray diffraction under a coating of perfluorinated oil and indexed, providing cell parameters consistent with the literature for these compounds. Under inert atmosphere conditions, crystals were gently crushed into powders and assessed by IR spectroscopy, which also confirmed the successful syntheses. The powders were packed under an inert atmosphere into ZrO_2 rotors for solid-state NMR experiments.

2.2. Solid-state NMR spectroscopy

SSNMR spectra were recorded at 9.4 T and 21.1 T using Bruker AVANCE III and Bruker AVANCE II spectrometers, respectively. A 4 mm cross-polarization magic angle spinning (CP/MAS) probe was used for ^1H and ^{13}C experiments at Larmor frequencies of $\nu(^1\text{H}) = 400.130$ and $\nu(^{13}\text{C}) = 100.613$ MHz, respectively. The ^{13}C CP/MAS NMR spectra were collected at spinning speeds of 8 or 11 kHz, and ^1H DUMBO [41]/MAS NMR spectra at 10 kHz spinning speed. The ^1H

and ^{13}C isotropic chemical shifts were calibrated using adamantane (^1H :1.85 ppm; central signal) and glycine (^{13}C :176.03 ppm; carbonyl signal) as external standards. The pulse calibration and final resolution of the ^1H DUMBO/MAS NMR spectrum of a glycine standard is described and shown in the Supporting information (Fig. S1). For ^{93}Nb NMR experiments, a 5 mm solenoid probe was used at a Larmor frequency of $\nu(^{93}\text{Nb}) = 97.936$ MHz. The CT-selective $\pi/2$ pulse length was $0.55\ \mu\text{s}$ and the recycle delay was 5 s. Static ^{93}Nb NMR spectra at 21.1 T were collected using a 4 mm CP/MAS probe ($\nu(^{93}\text{Nb}) = 220.317$ MHz). The CT-selective $\pi/2$ pulse length was $1.3\ \mu\text{s}$ and the recycle delay was 2 s. The ^{93}Nb isotropic chemical shift was calibrated using dilute NbCl_5 in dry acetone (^{93}Nb :0.0 ppm). Static ^{95}Mo NMR spectra were collected at 21.1 T using a 7 mm H/X low- γ probe ($\nu(^{95}\text{Mo}) = 58.661$ MHz). WURST-QCPMG [42] experiments were carried out using a $50\ \mu\text{s}$ WURST pulse, with 64 loops. The CT-selective $\pi/2$ pulse lengths in the solid echo experiment ($90^\circ\text{-}\pi\tau_{\text{R}}\text{-}90^\circ\text{-}\pi\tau_{\text{R}}\text{-acquire}$) were $3.0\ \mu\text{s}$ and the recycle delay was 5 s. The ^{95}Mo isotropic chemical shifts were calibrated using a 2 M aqueous solution of Na_2MoO_4 (^{95}Mo :0.0 ppm). High-power ^1H decoupling was used for all ^{13}C , ^{95}Mo , and ^{93}Nb experiments. All SSNMR experiments were performed at ambient laboratory temperatures (~ 295 K). NMR spectra were fit using the TopSpin 3.5 pl2 software package and WSolids [43]. The reported Euler angles follow the convention used in WSolids and as described in reference [44].

2.3. Density Functional Theory Computations

DFT calculations were first performed using CASTEP version 4.4, [45–47] implemented via Materials Studio, on crystal structure files obtained from the Cambridge Crystallographic Database Centre (CCDC). All NMR parameters were extracted from the CASTEP output files using EFGShield version 4.2. [44].

The crystal structure for the oxoniobium carboxylate (**1**) (CCDC entry number:1203302) was used as input to calculate (GGA PBE) NMR parameters for each of the niobium sites. The positions of the niobium ions and the hydrogen atoms were optimized prior to the calculation of niobium electric field gradient and magnetic shielding tensors. A series of calculations was performed by varying both the energy cut-off and the k -point sampling. At a $3\times 5\times 3$ k -point sampling with an energy cut-off of 610 eV, the NMR parameters showed negligible variation from the results of lower quality calculations, and are considered to be converged. Niobium magnetic shielding tensors were converted to chemical shift tensors using a linear regression analysis given by $\delta_{\text{iso}} = a(\sigma_{\text{iso}}^{\text{ref}} - \sigma)$, where $a = 0.997$ and $\sigma_{\text{iso}}^{\text{ref}} = -578.09$ ppm [24].

A series of single-point energy calculations (GGA PBE) was conducted on molybdenum acetate ($\text{Mo}_2(\text{O}_2\text{CH}_3)_4$) (**2**) (CCDC entry number:1213071) and molybdenum difluoroacetate ($\text{Mo}_2(\text{O}_2\text{CHF}_2)_4$) (**3**) in order to test the convergence of both the k -point sampling and the energy cut-off level. A diffraction structure of the latter is unavailable, so the structure of **2** was used as a template to create a structural model for **3**, whereby two of the hydrogen atoms on each terminal methyl group were manually changed to fluorine atoms. It was found that for both structures, using the GGA PBE functional and on-the-fly generated pseudopotentials, convergence was reached at an $8\times 8\times 8$ sampling with a cut-off energy of 750 eV and 650 eV for **2** and **3**, respectively. Geometry optimizations (partial, full, or none, as noted in the Supporting information) were then conducted on each of the molybdenum compound structures using the GGA PBE functional and on-the-fly generated pseudopotentials. Calculations of the molybdenum EFG and magnetic shielding tensors were performed at the same level of theory. Molybdenum magnetic shielding tensors were converted to chemical shift tensors using $\text{Mo}(\text{CO})_6$ as a standard reference using the conversion $\delta_{\text{iso}} = \sigma_{\text{iso}}^{\text{ref}} - \sigma + \delta^{\text{ref}}$, where $\sigma_{\text{iso}}^{\text{ref}} = 1572$ ppm and $\delta^{\text{ref}} = -1860$ ppm [33].

A second series of calculations is reported for these structures with the inclusion of relativistic effects. Cluster model calculations were conducted on individual molecules extracted from each of the crystal

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