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Observation of Solid-State ^{103}Rh NMR by Cross-Polarization

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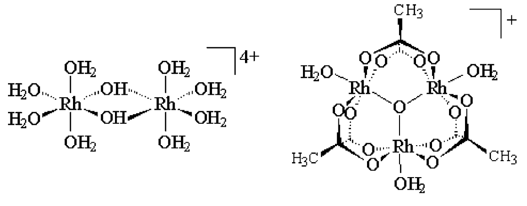
Considering the wide interest in the chemistry of Rh and its compounds, it is somewhat surprising that there have been no reports of the use of solid-state ^{103}Rh NMR spectroscopy to characterize nonmetallic Rh-containing solids. Although the ^{103}Rh isotope is 100% naturally abundant and dipolar ($I = 1/2$), it has a very small magnetogyric ratio (γ) and thus resonates at low frequency, yielding a very small signal for conventional NMR (20% that of natural abundance ^{13}C). Despite this low sensitivity, many studies have reported direct-observe ^{103}Rh NMR spectroscopic data for liquids,[1,2] which have proven very useful for molecular structure determination.[3] Although much progress has been made in solid-state NMR spectroscopy for some low-γ nuclei such as ^{89}Y and ^{109}Ag[4,5] and for other $I = 1/2$ nuclei in difficult systems,[6,7] a recent review[8] contained no data for ^{103}Rh. Complicating factors in the solid state likely include a very large chemical shift anisotropy (CSA) for all but the most symmetrical sites, which, combined with the low sensitivity, could make solid-state ^{103}Rh NMR spectroscopy difficult at best. A large CSA would further reduce sensitivity by distributing the intensity over a large number of spinning sidebands, possibly over a frequency range too large for uniform excitation. Use of CP methods is likely necessary for practical application of solid-state NMR for low-γ, $I = 1/2$ nuclei in many rigid diamagnetic systems. In addition to providing an increase in maximum signal intensity by a factor up to γ_{H-1}/γ_X (31 for X = ^{103}Rh), CP methods allow repetition periods on the order of ^{1}H T_1, typically a few seconds. The few T_1 measurements for low-γ nuclei in rigid diamagnetic systems range from several hundred to thousands of seconds,[9,10] confirming the impression that direct polarization is likely to be impractical in most cases.

Here we report ^{103}Rh[^{1}H] CP/MAS NMR data for two crystalline compounds containing polynuclear Rh(III) clusters; the mesitylate salt of the Rh dimer (**1**), $[(H_2O)_4Rh(\mu_2\text{-}OH)_2Rh(H_2O)_4]\cdot(dmtos)_4\cdot 8H_2O$, and the perchlorate salt of the oxo-centered acetate-bridged Rh trimer (**2**), $[Rh_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(OH_2)_3]ClO_4\cdot 2H_2O$ (Chart 1). The NMR spectra were obtained with a 400 MHz (9.4 T) Varian Inova spectrometer (12.76 MHz for ^{103}Rh), using a “T3”-type Varian/Chemagnetics sample probe assembly and “low-γ” tuning accessory. Samples were held in 7.5 mm (o.d.) rotors at 25 °C. Chemical shifts were measured with respect to an aqueous 0.5 mol L^{-1} solution of the $Rh(H_2O)_6^{3+}$ ion at $\delta_{iso} \equiv 9915.8$ ppm.[11] Experimental details for the NMR experiments are given as Supporting Information.

We found that ^{103}Rh[^{1}H] CP/MAS spectra can be readily observed from the mesitylate salt of **1** using conventional CP/MAS techniques at low to moderate spinning rates (Figure 1). These spectra show a broad spinning sideband pattern for the single crystallographic Rh site.[12] The isotropic chemical shift, $\delta_{iso} = 10\,131$ ppm, is downfield from the 9997.4 ppm value observed for **1** in aqueous solution.[11] The signal intensity varied smoothly with contact time over the range 4−20 ms, as expected for classical CP kinetics,[13] and reached a maximum near 8 ms (Figure 2). A best-fit cross-relaxation time of $T_{Rh-H} = 13 \pm 2$ ms was obtained by constraining the value for the ^{1}H relaxation time in the rotating frame, $T_{1\rho,H} = 7$ ms, which we measured by direct ^{1}H observation for this compound.

Chart 1. Rh Clusters Studied



1 **2**

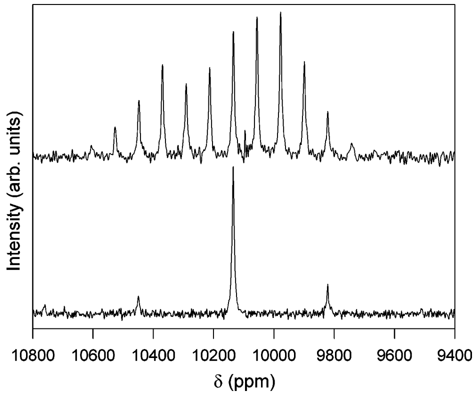


Figure 1. ^{103}Rh[^{1}H] CP/MAS NMR spectra of the mesitylate salt of **1** taken at spinning rates of 1.0 kHz (top) and 4.0 kHz (bottom). Both spectra acquired with 8-ms contact time, 5-s relaxation delay for 12 000 (top) and 15 800 (bottom) acquisitions.

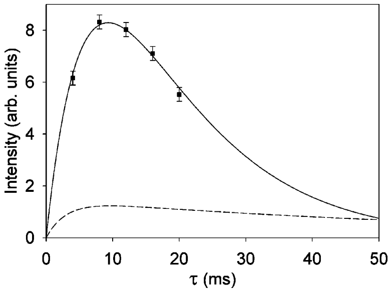


Figure 2. Variation of ^{103}Rh[^{1}H] CP/MAS intensity with contact time (τ) for the mesitylate salt of **1** (symbols) and a fit (solid line) assuming classical CP kinetics (see text). Dashed line is estimated curve for **2** at equivalent spin density.

Analysis of the spinning sideband intensities[14] at 1 kHz spinning rate gave CSA principal values of $\delta_{11} = 10\,551$, $\delta_{22} = 10\,048$,

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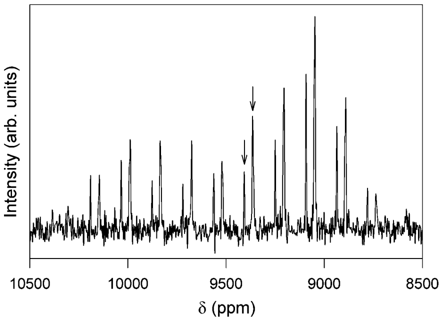

Figure 3. ^{103}Rh[^{1}H] CP/MAS spectrum of the perchlorate salt of **2**, acquired at a spinning rate of 2.0 kHz with 8-ms contact time and 5-s relaxation delay for 65 000 acquisitions. Arrows denote isotropic peaks.

and $\delta_{33} = 9793$ ppm, corresponding to a span of $\Omega = \delta_{11} - \delta_{33} = 758$ ppm and skew $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega = -0.33$. These values indicate an electron distribution that differs significantly from axial symmetry, consistent with the double hydroxyl-bridged geometry of **1**.

We also obtained CP/MAS spectra from the perchlorate salt of **2**, although with more difficulty than for the dimer salt. At a spinning rate of 2 kHz (Figure 3), two sets of spinning sidebands are clearly resolved with an approximate intensity ratio of 1:2. Closer inspection reveals that each of the more intense set of sidebands contains two poorly resolved peaks, consistent with the presence of three inequivalent Rh positions.[15] The chemical shifts for these three sites, $\delta_{iso} = 9401$, 9359, and 9354 ppm, are remarkably close to the measured value $\delta_{iso} = 9390$ ppm for **2** in aqueous solution.[16] Analysis of the spinning sidebands for the resonance at $\delta_{iso} = 9401$ ppm indicates a CSA characterized by $\Omega = 1720$ ppm and $\kappa = -0.64$. The resonances at $\delta_{iso} = 9359$ and 9354 ppm could not be analyzed separately, but treating their integrated intensities as a single resonance gave similar values of $\Omega = 1620$ ppm and $\kappa = -0.58$. The corresponding crystallographic sites have identical coordination geometry and could be expected to exhibit similar NMR parameters; in solution **2** yields a single ^{103}Rh NMR peak consistent with D_{3h} symmetry.[16] Comparison with data for the dimer indicates that the CSAs of the trimer are significantly larger but closer to axial symmetry, reflecting the general arrangement of ligands about the Rh center. The four oxygens of the acetate bridges are approximately equatorially arranged about an axis formed by the μ_3-O and η-OH$_2$ groups. Comparison with the CSA for the dimer salt indicates that the difference in δ_{iso} for the two clusters is mostly due to increased shielding for the trimer in the plane of the acetate bridges.

Our solid-state ^{103}Rh NMR results for the salts of **1** and **2** suggest guidelines for future studies, based on the strength of the ^{103}Rh$-^1$H dipolar coupling. A limiting factor for potential signal enhancement from conventional CP/MAS is the ratio $T_{Rh-H}/T_{1\rho,H}$, as has been noted previously.[17] For classical CP kinetics, the rate of polarization transfer, $(T_{Rh-H})^{-1}$, is proportional to the van Vleck second moment of the dipolar coupling, $M_{2[Rh-H]}$.[18] For this purpose, we redetermined the crystal structures of these compounds to include the hydrogen positions (see Supporting Information). From these structures, we calculate values of $M_{2[Rh-H]} = 0.15 \times 10^6$ Hz^2 for the dimer salt and 0.03×10^6 Hz^2 for the crystalline trimer, assuming rapid methyl group rotation. Assuming a linear dependence of $(T_{Rh-H})^{-1}$ with $M_{2[Rh-H]}$, the value $T_{Rh-H} = 13$ ms measured for the dimer salt yields a slope of about 0.51 ([ms^{-1}]/[10^6 Hz^2]) at our experimental conditions. From this slope, we estimate $T_{Rh-H} \approx 65$ ms for the trimer salt, which, combined with the measured $T_{1\rho,H} = 3$ ms for this compound, suggests that the maximum CP signal intensity attainable is about a factor of 7 less than for the dimer salt (Figure 2). Interestingly, our results suggest that very little intensity enhancement is available for **2** from CP and that the experimental advantage of CP in this case lies primarily in shortening the effective T_1. For other systems, if an estimate for the heteronuclear dipolar second moment can be obtained, then comparison with the present values and a measurement of $T_{1\rho,H}$ can suggest suitable experimental parameters for CP/MAS.

Having thus far used only modest B$_1$ fields and the most basic CP/MAS experiments at a relatively low field, we believe that further experimental improvements are possible, especially considering the relatively unfavorable $T_{1\rho,H}$ for our compounds. The broad CP match condition for the dimer salt should allow optimization of experimental parameters at higher spinning rates, which might be necessary at larger magnetic fields. Recently developed techniques for modulating the B$_1$ fields during CP, especially those[19] that increase $T_{1\rho,H}$ and decrease T_{Rh-H}, could be helpful for systems with unfavorable CP kinetics. Our results indicate that solid-state NMR spectroscopy should become a more useful, if time-consuming, technique for low-γ, $I = 1/2$ nuclei, even for ^{103}Rh.

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Supporting Information Available: Crystal structure data, synthesis methods, and experimental details of NMR and X-ray diffraction measurements (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Mann, B. E. *Annu. Rep. NMR Spectrosc.* **1991**, *23*, 141−207.
(2) Ernsting, J. M.; Gaemers, S.; Elsevier, C. J. *Magn. Reson. Chem.* **2004**, *42*, 721−736.
(3) Spiccia, L.; Aramini, J. M.; Crimp, S. J.; Drljaca, A.; Lawrenz, E. T.; Tedesco, V.; Vogel, H. J. *J. Chem. Soc., Dalton Trans.* **1997**, 4603−4609.
(4) Penner, G. H.; Li, W. L. *Inorg. Chem.* **2004**, *43*, 5588−5597.
(5) Bowmaker, G. A.; Harris, R. K.; Assadollahzadeh, B.; Apperley, D. C.; Hodgkinson, P.; Amornsakchai, P. *Magn. Reson. Chem.* **2004**, *42*, 819−826.
(6) Hung, I.; Rossini, A. J.; Schurko, R. W. *J. Phys. Chem. A* **2004**, *108*, 7112−7120.
(7) Siegel, R.; Nakashima, T. T.; Wasylishen, R. E. *J. Phys. Chem. B* **2004**, *108*, 2218−2226.
(8) Smith, M. E. *Annu. Rep. NMR Spectrosc.* **2001**, *43*, 121−175.
(9) Harazono, T.; Watanabe, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2383−2388.
(10) Florian, P.; Gervais, M.; Douy, A.; Massiot, D.; Coutures, J. P. *J. Phys. Chem. B* **2001**, *105*, 379−391.
(11) Read, M. C.; Glaser, J.; Sandstrom, M.; Toth, I. *Inorg. Chem.* **1992**, *31*, 4155−4159.
(12) Cervini, R.; Fallon, G. D.; Spiccia, L. *Inorg. Chem.* **1991**, *30*, 831−836.
(13) Kolodziejski, W.; Klinowski, J. *Chem. Rev.* **2002**, *102*, 613−628.
(14) Eichele, K.; Wasylishen, R. E. *WSOLIDS*, 2.0.18; Dalhousie University: Halifax, Canada, 2000.
(15) Glowiak, T.; Kubiak, M.; Szymanskabuzar, T. *Acta Crystallogr., Sect. B* **1977**, *33*, 1732−1737.
(16) Houston, J. R.; Yu, P.; Casey, W. H. *Inorg. Chem.* **2005**, *44*, 5176−5182.
(17) Sebald, A. *NMR* **1994**, *31*, 91−131.
(18) Mehring, M. *Principles of High-Resolution NMR in Solids*, 2nd ed.; Springer-Verlag: Berlin, 1983.
(19) Fu, R. Q.; Hu, J.; Cross, T. A. *J. Magn. Reson.* **2004**, *168*, 8−17.

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