Observation of solid-state [103]Rh NMR by cross-polarization

Brian L. Phillips[1*], Jacqueline R. Houston[2], Jian Feng[3], William H. Casey[2,4]

Supporting Information

[1]Department of Geosciences, State University of New York, Stony Brook, NY 11794

[2]Department of Chemistry, University of California, Davis, CA 95616, USA.

[3]Department of Chemistry, State University of New York, Stony Brook, NY 11794,

[4]Department of Geology, University of California, Davis, CA 95616, USA;

[*]brian.phillips@stonybrook.edu

Sample preparation

The mesitylate salt of the hydroxyl-bridged rhodium(III) dimer
$[(H_2O)_4Rh(\mu_2\text{-}OH)_2Rh(H_2O)_4]\cdot(dmtos)_4\cdot 8H_2O$ (**I**) was crystallized from a solution prepared by
dissolution of the active hydroxide, using a slight excess of 2-mesitylene sulfonic acid as
described by Cervini et al [1]. Crystals of the perchlorate salt of the oxo-centered acetate-bridged
Rh(III) trimer (Fig. 1b) $[Rh_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(OH_2)_3]ClO_4\cdot 2H_2O$ (**II**) were prepared by
dissolving the Rh(III) active hydroxide in excess acetic acid, which was then heated at 333 K
overnight, purified in a cation exchange column and allowed to crystallize upon slow
evaporation [2]. The identity of both compounds was confirmed by comparison of the cell
parameters determined by X-ray diffraction with published structures. A standard solution of
$Rh(H_2O)_6^{3+}(aq)$ was prepared by dissolving the appropriate amount of Rh(III) active hydroxide
in $HClO_4$ to give a final $[H^+] = 1$ M and $[Rh^{3+}] = 0.5$ M.

NMR spectroscopy

The NMR experiments were conducted on a 400 MHz (9.4 T) Varian Inova spectrometer
operating at 12.76 MHz for ^{103}Rh and 399.76 MHz for ^{1}H. We used a "T3"-type
Varian/Chemagnetics sample probe configured for 7.5 mm (outside diameter) rotors with a
Varian "low-γ" tuning accessory. All spectra were taken at 25°C. Initial pulse power was
calibrated on the solid sample for ^{1}H and on an aqueous 0.5 mol L^{-1} solution of the $Rh(H_2O)_6^{3+}$
ion for ^{103}Rh, which also served as the chemical shift reference at $\delta_{iso} \equiv 9915.8$ ppm. The tuning
of the ^{103}Rh channel did not change significantly upon replacement of the solution standard with
solid samples. The CP/MAS spectra were collected with standard pulse sequences using CW
irradiation at the first side-band match condition with $\nu_{1,Rh} = 12.5$ kHz and $\nu_{1,H} \approx \nu_{1,Rh} + \nu_{rot}$.
These conditions required approximately 230 watts of RF input power to the ^{103}Rh channel. The

match curve for the dimer salt appeared reasonably broad, ca. 8-10 kHz full-width at half-height, and could be measured in a few hours, making the dimer salt a useful set-up material.   Initial set-up at the Hartmann-Hahn match ($\nu_{1,H} = \nu_{1,Rh} = 12.5$ kHz) was accomplished by independent calibration of each channel through direct [1]H- and [103]Rh-observation.   For CP, the initial ^{1}H excitation was a 6 μs pulse at $\nu_{1,H} = 40$ kHz.   For the CP/MAS spectra, the total pre-acquisition delay was 75 μs (40 kHz spectral window). The resulting time-domain data were shifted -50 μs (2 complex points) then the first 100 μs (4 complex points) re-calculated by linear prediction prior to transformation to the frequency domain.

The ^{1}H relaxation times $T_{1\rho,H}$ and $T_{2,H}$ were measured by direct observation under non-spinning conditions, using a Chemagnetics probe assembly configured for 4 mm rotors and low ^{1}H background signal.   Initial ^{1}H excitation and spin echoes used $\nu_{1,H} = 62.5$ kHz ($\pi/2 = 4$ μs). The [1]H $T_{1\rho}$'s were measured at $\nu_{1,H} = 12.5$ kHz, the same field as used for the CP/MAS measurements.

Crystal structure determination

[(H₂O)₄Rh(μ₂-OH)₂Rh(H₂O)₄] ·(dmtos)₄·8H₂O (**I**)
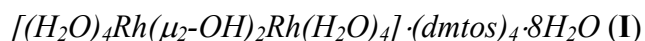
A light yellow block of (**I**) with approximate orthogonal dimensions 0.32 x 0.26 x 0.17mm³ was placed and optically centered on the Bruker APEXII[5] CCD system at –183(2)°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Five ω-scan data frame series were collected [MoKα] with 0.3° wide scans, 20 seconds per frame and 606 frames collected per series at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). The crystal to detector distance was 4.97cm, thus

providing a complete sphere of data to $2\theta_{max}$=61.14°. A total of 57541 reflections were collected

and corrected for Lorentz and polarization effects and absorption using Blessing's method as

incorporated into the program SADABS[6,7] with 9054 unique. The SHELXTL[8] program package

was implemented to determine the probable space group and set up the initial files. System

symmetry, systematic absences and intensity statistics indicated the centrosymmetric monoclinic

non-standard space group $P2_1/c$ (no. 14). The structure was determined by direct methods with

the successful location of a majority of the molecule of interest within the asymmetric unit using

the program XS[9]. The structure was refined with XL[9]. The 57541 data collected were merged

based upon identical indices yielding 33830 data [R(int)=0.0165] that were truncated to

$2\theta_{max}$=60.00° resulting in 31381 data that were further merged during least-squares refinement to

8183 unique data [R(int)=0.0149]. A single least-squares difference-Fourier cycle was required

to locate the remaining non-hydrogen atoms and additional difference-Fourier maps were

required to locate the hydrogen atoms present. All non-hydrogen atoms were refined

anisotropically. Hydrogen atoms were allowed to refine freely throughout the refinement. The

final structure was refined to convergence [$\Delta/\sigma \leq 0.006$] with R(F)=1.94%, wR(F^2)=4.77%,

GOF=1.096 for all 8183 unique reflections [R(F)=1.89%, wR(F^2)=4.73% for those 8004 data

with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure

is both correct and complete.

[Rh$_3$(μ_3-O)(μ-OOCCH$_3$)$_6$(OH$_2$)$_3$]ClO$_4$·2H$_2$O (**II**)
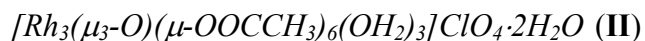
An orange plate of (**II**) with approximate orthogonal dimensions 0.49 x 0.19 x 0.06mm^3

was placed and optically centered on the Bruker SMART1000[5] CCD system at −183(2)°C. The

initial unit cell was indexed using a least-squares analysis of a random set of reflections collected

from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Five ω-scan data frame series were collected [MoKα] with 0.3° wide scans, 20 seconds per frame and 606 frames collected per series at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). The crystal to detector distance was 4.123cm, thus providing a complete sphere of data to $2\theta_{max}$=61.14°. A total of 49838 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[6,7] with 7970 unique.

The SHELXTL[8] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the centrosymmetric monoclinic non-standard space group $P2_1/c$ (no. 14). The structure was determined by direct methods with the successful location of a majority of the molecule of interest within the asymmetric unit using the program XS[9]. The structure was refined with XL[9]. The 49838 data collected were merged based upon identical indices yielding 29624 data [R(int)=0.0246] that were truncated to $2\theta_{max}$=60.00° resulting in 28476 data that were further merged during least-squares refinement to 7369 unique data [R(int)=0.0293]. A single least-squares difference-Fourier cycle was required to locate the remaining non-hydrogen atoms and additional difference-Fourier maps were required to locate the hydrogen atoms present. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were allowed to refine freely throughout the refinement. The final structure was refined to convergence [$\Delta/\sigma \leq 0.002$] with R(F)=3.14%, wR(F2)=5.44%, GOF=1.092 for all 7369 unique reflections [R(F)=2.22%, wR(F2)=5.04% for those 6178 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. Due to β = 90.004(1)° an

additional investigation into the cell symmetry was performed using Cellnow[10], Rlatt[8], Lepage[11]

and Platon[12]; all of which confirmed the current unit cell to be correct.

References

1. Cervini, R.; Fallon, G. D.; Spiccia, L., *Inorg. Chem.* **1991,** *30*, 831-836.
2. Houston, J. R.; Yu, P.; Casey, W. H., *Inorg. Chem.* **2005,** *44*, 5176-5182.
3. Hung, I.; Rossini, A. J.; Schurko, R. W., *J. Phys. Chem. A* **2004,** *108*, 7112-7120.
4. Siegel, R.; Nakashima, T. T.; Wasylishen, R. E., *J. Phys. Chem. B* **2004,** *108*, 2218-2226
5. Bruker (2004) SMART (Version 5.054) and SAINT (Version 7.16b). Bruker AXS Inc., Madison, Wisconsin, USA.
6. Blessing, R. H., *Acta Cryst. A* **1995**, *51*, 33-38.
7. Sheldrick, G.M., SADABS (2003) Version 2.10, 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany.
8. Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.
9. Sheldrick, G. M., (1997). SHELXS97 and SHELXL97. Universität Göttingen: Göttingen, Germany.
10. Sheldrick, G.M., (private communication) CELLNOW, Twin matrix determination program, Universität Göttingen: Göttingen, Germany, 2003.
11. Spek, A.L., Determination of the metrical symmetry of a lattice following an algorithm published by Y. LePage (NRC-Ottawa/Canada).
12. Spek, A.L., *J.Appl.Cryst.* **2003**, *36*, 7-13.