

ELECTRONIC SUPPLEMENTARY INFORMATION

**Non-Covalent Matere Bonds in Perrhenates Probed via Ultrahigh Field Rhenium-
185/187 NMR and Zero-Field NQR Spectroscopy**

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1. Experimental Details: NMR and NQR Spectroscopy

Solid-state $^{185/187}\text{Re}$ NMR at 18.8T

The $^{185/187}\text{Re}$ static NMR spectra were collected at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida using Bruker Avance III-HD and NEO spectrometer operating at $B_0 = 18.8$ T and a 4 mm low-E $^1\text{H}/\text{X}$ static probe designed and constructed at the NHMFL. The $^{185/187}\text{Re}$ pulse lengths used for experiments were calibrated directly using melaminium perrhenate. The QCPMG (quadrupolar Carr–Purcell–Meiboom–Gill) sequence of identical excitation and refocusing pulses was used to acquire multiple echoes for sensitivity enhancement. Due to the very rapid $^{185/187}\text{Re}$ spin-spin relaxation in these materials, the Wideband Uniform Rate Smooth Truncation-Carr-Purcell-Meiboom-Gill (WURST-CPMG) was not used. Typical parameters used for these experiments were as follows: $\pi/2 = 0.7$ to 1 μs ; $\tau_1 = 5.6$ to 15.6 μs ; recycle delay = 10 ms; number of echoes = 18 to 39 ; spectral window = 5 MHz, and number of transients = 10240 to 204800 . Variable offset cumulative spectrum data acquisition methods (VOCS) were used to cover the full powder pattern breadth of the final $^{185/187}\text{Re}$ SSNMR spectra. The number of sub-spectra ranging from 73 to 107 were acquired with VOCS offset varied from 150 to 200 kHz. For further details, see Table S1.

Solid-state $^{185/187}\text{Re}$ NMR at 35.2 T

The $^{185/187}\text{Re}$ static NMR experiments were performed on a 35.2 T Series-Connected Hybrid (SCH) NMR magnet designed and built at the NHMFL. The SCH NMR spectrometer was equipped with a Bruker Avance NEO console and a 4 mm $^1\text{H}/\text{X}$ double resonance static probe developed and built at the NHMFL. The QCPMG (Quadrupolar Carr–Purcell–Meiboom–Gill) sequence of identical excitation and refocusing pulses was used to acquire multiple echoes for sensitivity enhancement. Typical parameters used for these experiments were as follows: $\pi/2 = 1$ μs ; $\tau_1 = 3.5$ to 6.5 μs ; recycle delay = 15 ms; number of echoes = 24 to 30 ; spectral window = 2.5 MHz, and number of transients = 3072 to 16384 . For the SCH magnet, the conventional frequency-stepped VOCS method is not feasible due to the restricted tuning access for safety reasons when the magnet is above 18 T. Therefore, the powder pattern was reconstructed by fixing the transmitter

frequency and stepping the magnetic field. The sub-spectra were acquired with B_0 field increment steps varied from 0.013 T to 0.033 T, which correspond to changes in Larmor frequency ranging from 125 to 313 kHz. For further details, see Table S1.

Spectral fitting was carried out using QUEST software (see main text). Errors in each fitted parameter were assessed heuristically by systematic bidirectional variation while holding other parameters constant at their best-fit values.

All $^{185/187}\text{Re}$ experiments used the ^{17}O NMR resonance of aqueous D_2O as a secondary reference using the $^{185/187}\text{Re}/^{17}\text{O}$ spectrometer frequency (SF) interconversion: $\text{SF}(^{187}\text{Re}) = \text{SF}(^{17}\text{O}) \times 22.751600/13.556457$ or $\text{SF}(^{185}\text{Re}) = \text{SF}(^{17}\text{O}) \times 22.524600/13.556457$ (frequency ratios calculated from the magnetogyric ratios). $\Xi\%$ is ratio of the resonance frequency of the reference to that of the protons of TMS at infinite dilution in CDCl_3 ($\Xi\%(^{17}\text{O})=13.556457$; $\Xi\%(^{185}\text{Re})=22.524600$; $\Xi\%(^{187}\text{Re})=22.751600$).

Solid-state $^{185/187}\text{Re}$ nuclear quadrupole resonance (NQR)

All experiments were carried out at the National High Magnetic Field Laboratory (NHMFL, Tallahassee, Florida, USA) using a Bruker Avance NEO console and 4 mm HX static probe designed and constructed at the NHMFL. All spectra were acquired at room temperature using the spin echo pulse sequence with excitation and refocusing pulse length of 1 μs and 2 μs respectively. While searching for $^{185/187}\text{Re}$ NQR signals, the radiofrequency transmitter was varied with an offset of 200 kHz until a particular resonance was detected. Interpulse delay varied from 10.5 to 24.3 μs , and number of transients ranged from 10240 to 227328.

Table S1. Detailed $^{185/187}\text{Re}$ SSNMR experimental acquisition parameters

	$\pi/2$ / μs	τ_1 / μs	number of echoes	transients	recycle delay / ms	frequency step / kHz	Number of sub- spectra
18.8 T							
1	0.7	15.6	24	10240	10	150	85
2	0.7	15.6	31	10240	10	150	79
3	0.7	15.6	24	10240	10	150	107
4	0.7	5.6	39	40960	10	198	75
5	1	6.5	18	204800	10	187	73
35.2 T							
1	1	6.3	30	16387	15	312	38
2	1	6.3	30	7168	15	312	40
3	1	6.5	27	3072	15	178	80
4	1	3.5	29	10240	15	125	73
5	1	5.5	24	15360	15	208	56

Table S2. Experimental $^{185/187}\text{Re}$ quadrupolar coupling parameters obtained from $^{185/187}\text{Re}$ NQR

	$\nu_1(^{187}\text{Re})$ / MHz	$\nu_2(^{187}\text{Re})$ / MHz	$\nu_1(^{185}\text{Re})$ / MHz	$\nu_2(^{185}\text{Re})$ / MHz	$ C_Q(^{187}\text{Re}) $ / MHz	η	$ C_Q(^{185}\text{Re}) $ / MHz	η
1	40.755 (12)	44.664 (32)	43.293 (20)	46.686 (3)	165.86 (9)	0.890 (19)	173.91 (5)	0.909 (19)
2	44.688 (2)	49.334 (13)	46.683 (3)	51.888 (10)	182.94 (2)	0.881 (7)	192.16 (2)	0.873 (7)
3	48.273 (3)	62.810 (47)	51.531 (11)	65.667 (54)	225.68 (14)	0.693 (24)	236.88 (17)	0.717 (24)

2. Additional NQR Spectra

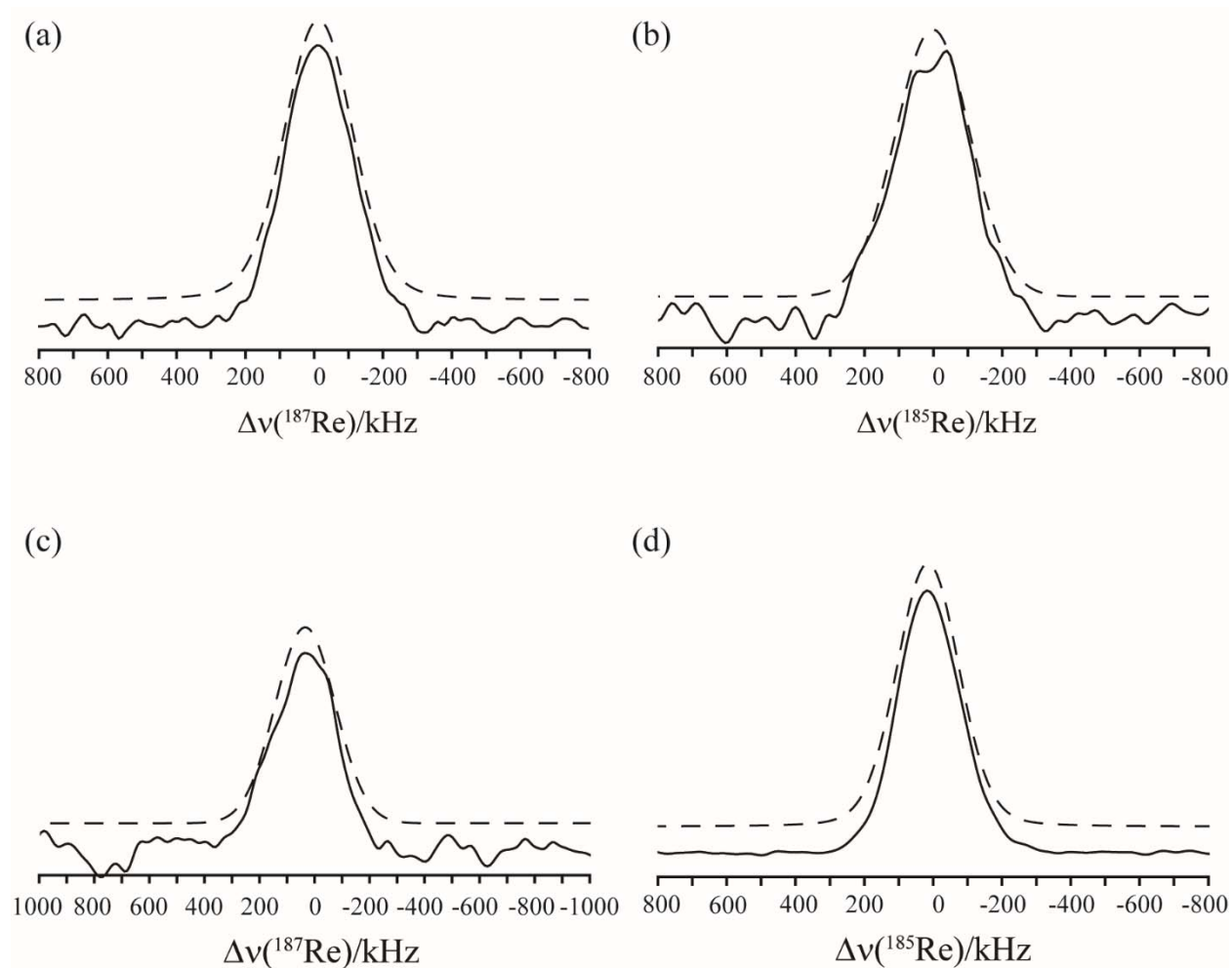


Figure S1. Experimental (solid black traces) and simulated (dashed black traces) ^{187}Re (a, c) and ^{185}Re (b, d) NQR spectra of powdered compound **1**, acquired with the transmitter on resonance at room temperature. The corresponding Lorentzian fits were simulated using ssNake. The ^{187}Re transition frequencies are: $\nu_1(m_I = \pm 1/2 \leftrightarrow \pm 3/2) = 40.755$ MHz (a) and $\nu_2(m_I = \pm 3/2 \leftrightarrow \pm 5/2) = 44.664$ MHz (c), where for all transitions $|\Delta m_I| = 1$. The ^{185}Re transition frequencies are: $\nu_1(m_I = \pm 1/2 \leftrightarrow \pm 3/2) = 43.293$ MHz (b) and $\nu_2(m_I = \pm 3/2 \leftrightarrow \pm 5/2) = 46.686$ MHz (d), where for all transitions $|\Delta m_I| = 1$.

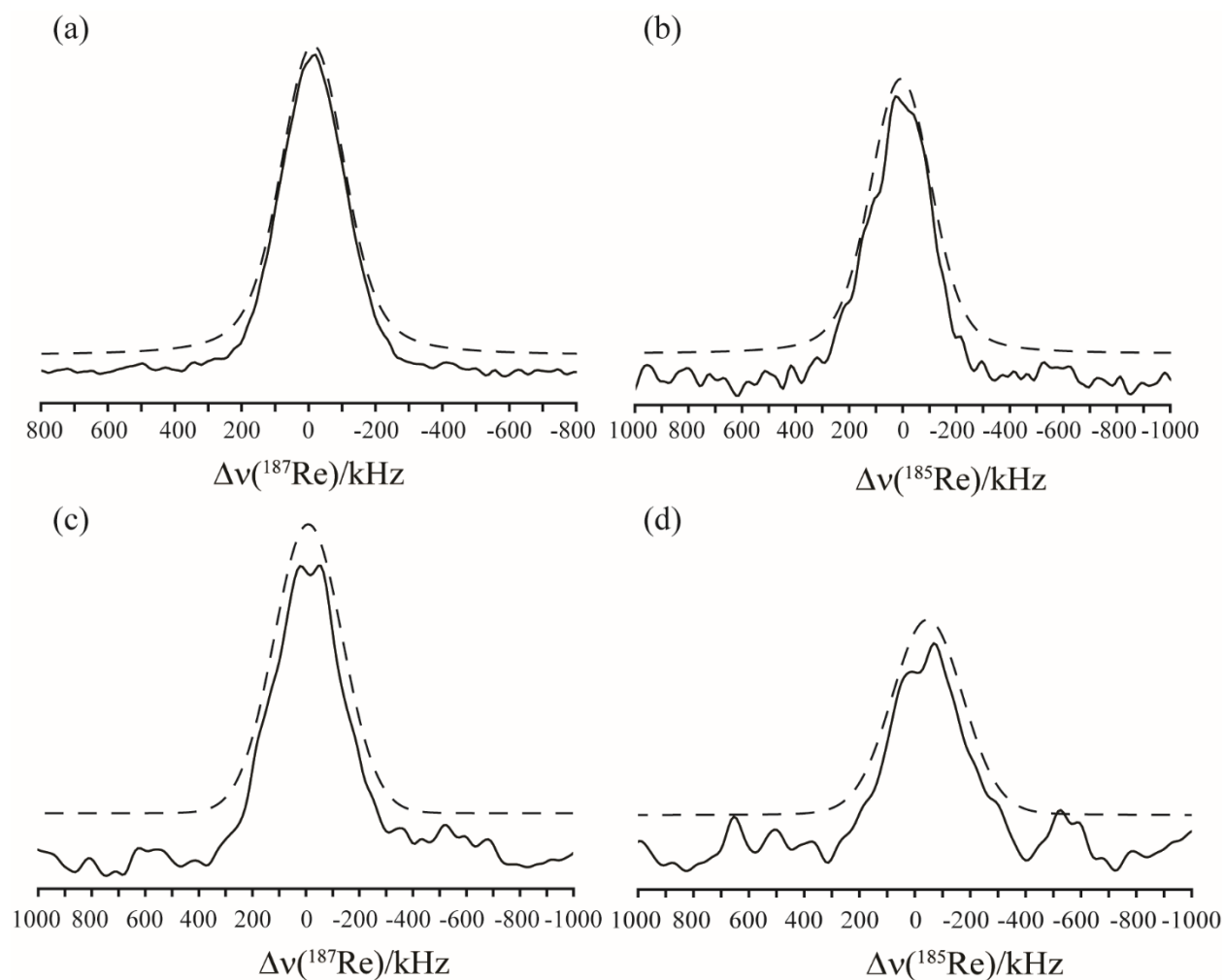


Figure S2. Experimental (solid black traces) and simulated (dashed black traces) ^{187}Re (a, c) and ^{185}Re (b, d) NQR spectra of powdered compound **3**, acquired with the transmitter on resonance at room temperature. The corresponding Lorentzian fits were simulated using ssNake. The ^{187}Re transition frequencies are: $\nu_1(m_I = \pm 1/2 \leftrightarrow \pm 3/2) = 48.273$ MHz (a) and $\nu_2(m_I = \pm 3/2 \leftrightarrow \pm 5/2) = 62.810$ MHz (c), where for all transitions $|\Delta m_I| = 1$. The ^{185}Re transition frequencies are: $\nu_1(m_I = \pm 1/2 \leftrightarrow \pm 3/2) = 51.537$ MHz (b) and $\nu_2(m_I = \pm 3/2 \leftrightarrow \pm 5/2) = 65.667$ MHz (d), where for all transitions $|\Delta m_I| = 1$.

3. Sample Preparation

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, TCI, abcr GmbH) and used without further purification.

Compounds **1**, **2**, and **3**, previously reported, were prepared according to the described procedure.^[1S] Compounds **4** and **5** were prepared following the same experimental protocol. Specifically, pyridine hydrochloride (for compound **4**) or acetylcholine hydrochloride (for compound **5**), were dissolved in isopropanol. An equimolar amount of Ag₂ReO₄ was then added to the solution. A whitish solid starts to precipitate immediately. The solution is filtered after 12 hours and the liquid is left to slowly evaporate in a clear borosilicate vial at room temperature. The resulting crystalline precipitate was gently grinded to perform solid-state NMR studies. Crystals of **5** suitable for single crystal X-ray diffraction formed after a few days.

4. X-Ray Diffraction

Data collection for **5** was performed at the XRD2 beamline of the Elettra Synchrotron, Trieste (Italy).^[2S] The crystals were dipped in NHV oil (Jena Bioscience, Jena, Germany) and mounted on the goniometer head with kapton loops (MiTeGen, Ithaca, USA). Complete datasets were collected at 100 K (nitrogen stream supplied through an Oxford Cryostream 700) through the rotating crystal method. Data were acquired using monochromatic wavelength of 0.620 Å on Pilatus 6M hybrid-pixel area detectors (DECTRIS Ltd., Baden-Daettwil, Switzerland). The diffraction data were indexed and integrated using XDS.^[3S] Crystals grew as tiny needles, in a triclinic crystal form, extremely sensitive to radiation damage. A complete dataset couldn't be obtained from a single crystal therefore two partial wedges have been merged using CCP4-Aimless^[4S,5S] code. The structure was solved by the dual space algorithm implemented in the SHELXT code.^[6S] Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F² implemented in SHELXL (Version 2019/3)^[7S]. The Coot program was used for modeling.^[8S] Anisotropic thermal motion refinement have been applied to all atoms. Hydrogen atoms were included at calculated positions with isotropic $U_{\text{factors}} = 1.2 \cdot U_{\text{eq}}$ or $U_{\text{factors}} = 1.5 \cdot U_{\text{eq}}$ (for methyl groups; U_{eq} being the equivalent isotropic thermal factor of the bonded non hydrogen atom). Thermal and geometric restrains (SIMU, SADI, DFIX, DANG) have been used to compensate artifacts of noisy electron density areas induced by radiation damage. A minor non-

merohedral twinning pathology has also been identified with Platon TWINROTMAT^[9S] routine and taken into account (i.e. model has been refined as two domains related by a 180° rotation around (2 1 1) lattice direction). Pictures were prepared using CCDC Mercury^[10S] software. Essential crystal and refinement data are reported in Table S3.

Table S3. Crystallographic data and refinement details for **5**.

CCDC Number	2289494
Chemical Formula	[C ₇ H ₁₆ NO ₂](ReO ₄)
Formula weight	396.41 g/mol
Temperature	100(2) K
Wavelength	0.620 Å
Crystal system	Triclinic
Space Group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 7.313(2) Å <i>b</i> = 8.956(2) Å <i>c</i> = 10.153(2) Å <i>α</i> = 79.13(3)° <i>β</i> = 71.47(3)° <i>γ</i> = 67.85(3)°
Volume	582.2(3) Å ³
Z	2
Density (calculated)	2.261 g·cm ⁻³
Absorption coefficient	7.282 mm ⁻¹
F(000)	376
Theta range for data collection	2.2° to 27.8°
Index ranges	-7 ≤ <i>h</i> ≤ 8, -9 ≤ <i>k</i> ≤ 10, -8 ≤ <i>l</i> ≤ 11
Resolution	0.86 Å
Reflections collected	4770
Independent reflections	1814, 1534 data with <i>I</i> > 2σ(<i>I</i>)
Data multiplicity (max resltn)	2.01 (1.94)
<i>I</i> /σ(<i>I</i>) (max resltn)	15.02 (11.14)
R _{merge} (max resltn)	0.1489 (0.1772)
Data completeness (max resltn)	96.1% (95.4%)
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1814 / 107 / 137
Goodness-of-fit on F ²	1.117
Δ/σ _{max}	0.000
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.1033, wR ₂ = 0.1802
R indices (all data)	R ₁ = 0.1151, wR ₂ = 0.1859
Largest diff. peak and hole	6.573 and -4.117 eÅ ⁻³
R.M.S. deviation from mean	0.636 eÅ ⁻³

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

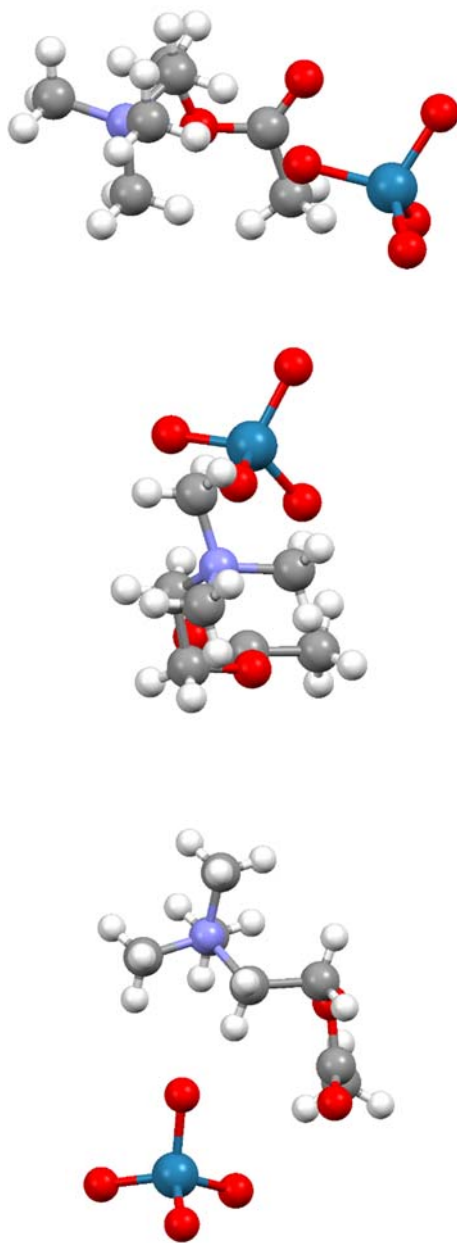


Figure S3. Ellipsoids representation (50% probability) of compound **5**. View along axis *a* (top), *b* (middle), *c* (bottom). Colour code: white, hydrogen; grey, carbon; red, oxygen; indigo, nitrogen; bluish, rhenium.

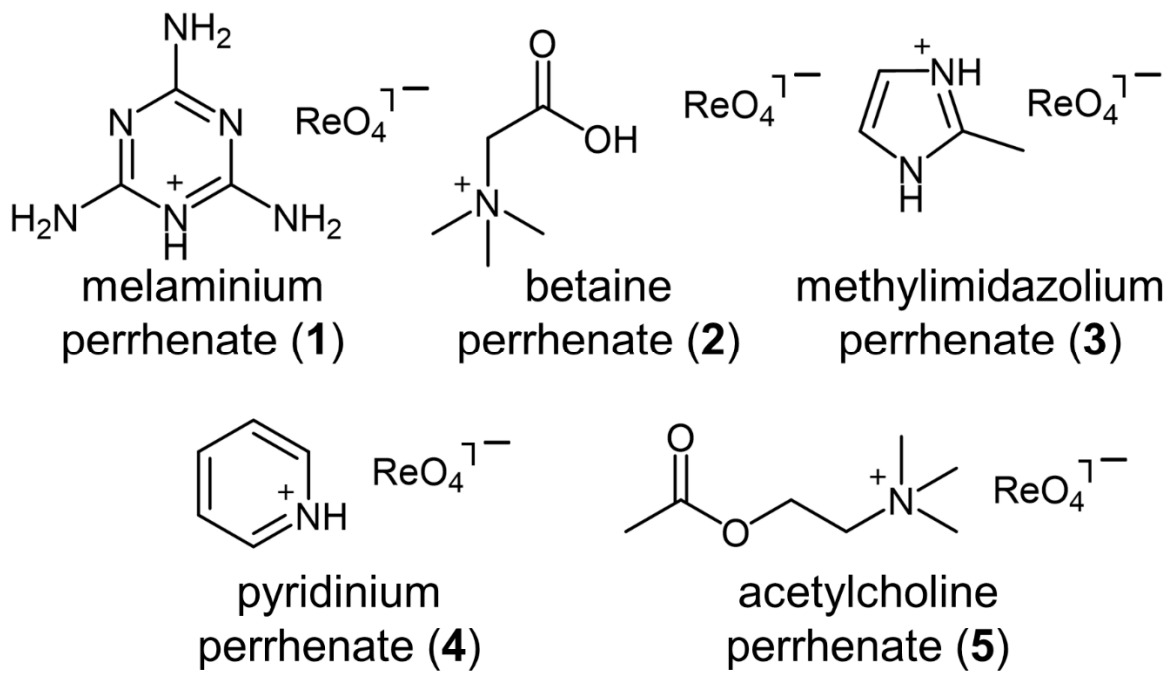


Figure S4. Structure of perrhenate salts studied herein.

5. References

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