

Supporting Information

An uncommon highly oxidized multiple bonded Re_2^{8+} species

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Experimental

Unless otherwise noted, the synthesis was carried out under an inert atmosphere using standard Schlenk techniques. Commercially available starting materials such as $(\text{Bu}^n_4\text{N})_2\text{Re}_2\text{Cl}_8$ and silver triflate were purchased from Sigma-Aldrich and used as received. The rhenium precursor $\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2$ was prepared using a published method.ⁱ Solvents were dried using a Glass Contour solvent system. Elemental analyses were performed by Robertson Microlit, Madison, NJ on material that had been placed under vacuum for three days. The infrared spectrum was recorded on a Perkin-Elmer 16PC FT IR spectrophotometer using KBr pellets. The electronic spectrum was recorded on a Shimadzu UV-2501 PC spectrophotometer. Electrochemical measurements were carried out in 0.1 M $\text{Bu}^n_4\text{NPF}_6$ solution in CH_2Cl_2 using a CH Instruments Model-CH1620A electrochemical analyzer with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, and operated with a scan rate of 100 $\text{mV}\cdot\text{s}^{-1}$. Potentials are referenced to the Ag/AgCl electrode. ^1H NMR data were recorded on a Mercury 300 spectrometer with chemical shifts referenced to the protonated solvent residue.

Synthesis of $\{[\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2](\text{O}_3\text{SCF}_3)_2\}$, **1.** To a flask charged with a solution of 41 mg (0.16 mmol) of $\text{Ag}(\text{SO}_3\text{CF}_3)$ in 20 mL of methylene chloride was added 100 mg (0.080 mmol) of $\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2$ dissolved in 10 mL of methylene chloride. The color of the supernatant liquid changed immediately from purple to green. The reaction mixture was stirred at ambient temperature for 2 h and then filtered to remove a dark-colored silver residue. After removal of the solvent under vacuum, a deep green solid was obtained in essentially quantitative yield. Anal. Calcd for

$C_{32}H_{48}N_{12}S_4O_{12}F_{12}Re_2$: C, 25.26; H, 3.18; N, 11.05%. Found: C, 25.09; H, 3.54; N, 11.27%. 1H NMR ($CDCl_3$, ppm): 3.37 (m, 32H), 2.04 (m, 16H).

Synthesis of $\{[Re_2(hpp)_3(OH)(O_3SCF_3)]_2(\mu-O)_2\}(O_3SCF_3)_2 \cdot 4CH_2Cl_2, 2 \cdot 4CH_2Cl_2$. This was done similarly to that of **1** but once the silver residue was filtered off the volume of the filtrate was reduced to ca. 15 mL and then a layer of previously deoxygenated but un-dried hexanes was carefully placed on top of the solution. After two weeks, dark brownish-green crystals were collected by filtration, and washed with dry hexanes. Yield: 83 mg, 80%. Anal. Calcd for $C_{46}H_{74}N_{18}S_4O_{16}F_{12}Re_4$: C, 24.70; H, 3.33; N, 11.27%. Found: C, 24.54; H, 3.38, N, 11.50%. IR (cm^{-1}): 3316 (s), 2960 (m), 2863 (m), 1630 (m), 1553 (s), 1476 (m), 1385 (s), 1316 (s), 1223 (s), 1161 (m), 1029 (s), 909 (m), 766 (m), 637 (m). 1H NMR ($CDCl_3$, ppm): 3.25 (m, 48H), 1.95 (m, 24H), 1.17 (s, 2H). 1H NMR (C_6D_6): 2.61 (m, 24H), 2.05 (m, 24H), 1.04 (m, 24H), 0.91 (s, 2H). UV-vis (λ_{max} , nm): 260, 359, 441 and 606.

X-ray Structure Determination. Diffraction data were collected at 213 K on a Bruker SMART 1000 CCD area detector system using omega scans of 0.3 deg/frame with exposition of 40 sec/frame. Cell parameters were determined using the SMART software suite.ⁱⁱ Data reduction and integration was performed with the SAINT.ⁱⁱⁱ An absorption correction was applied using the program SADABS.^{iv} Positions of the Re atoms were located via direct methods with the aid of the program SHELXTL.^v Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions. All hydrogen atoms were included in the calculation of the structure factors. Non-hydrogen atoms were refined with anisotropic displacement parameters. Four sections of the structure showed some degree of disorder. This was handled as follows: a) a carbon atom in a methylene group of one of the hpp ligands was refined with partial occupancies of 0.62384 and 0.37616; b) three interstitial CH_2Cl_2 molecules presented disorder and it was resolved by refinement using partial occupancies; c) two oxygen atoms of a triflate

ligand that was bound to a rhenium atom were refined with partial occupancies of 0.54272 and 0.45728;
d) a sulfur and two oxygen atoms in an unbound triflate anion were refined with partial occupancies of 0.52112 and 0.47888. For **2**, the structure was solved in the triclinic space group $P\bar{1}$. Selected bond distances and angles are listed in Table 1 and crystallographic data are provided in Table 2.

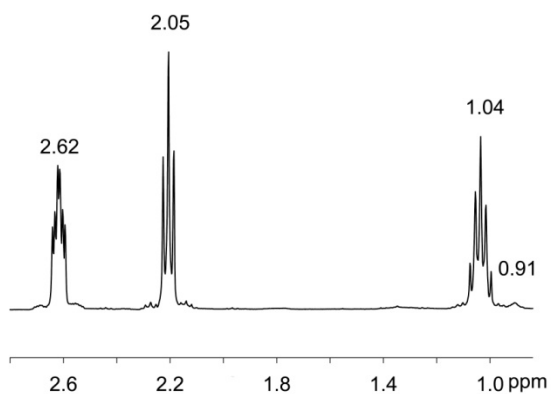


Fig S1 ^1H NMR spectrum of **2** in C_6D_6 .

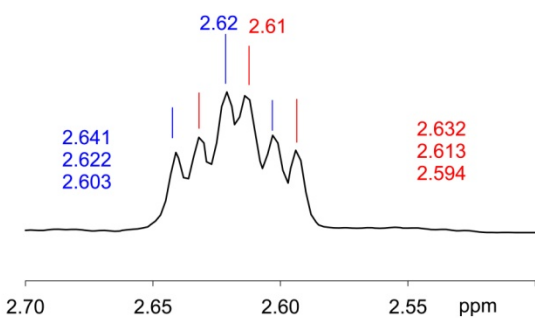


Fig S2 Expansion of the signal centered at 2.61-2.62 ppm in the ^1H NMR spectrum of **2** in C_6D_6 .

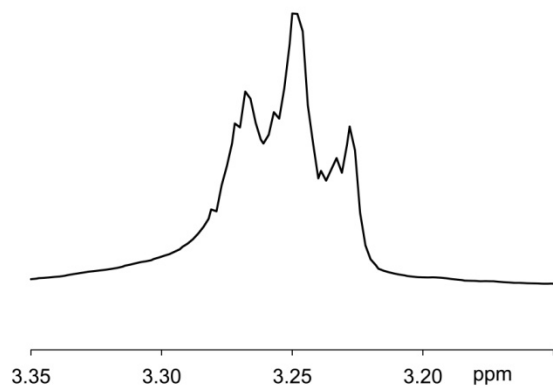


Fig S3 Expansion of the signal centered at ~ 3.35 ppm in the ^1H NMR spectrum of **1** in CDCl_3 .

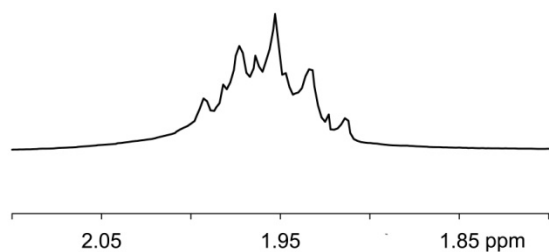


Fig S4 Expansion of the signal centered at ~1.95 ppm in the ¹H NMR spectrum of **1** in CDCl₃.

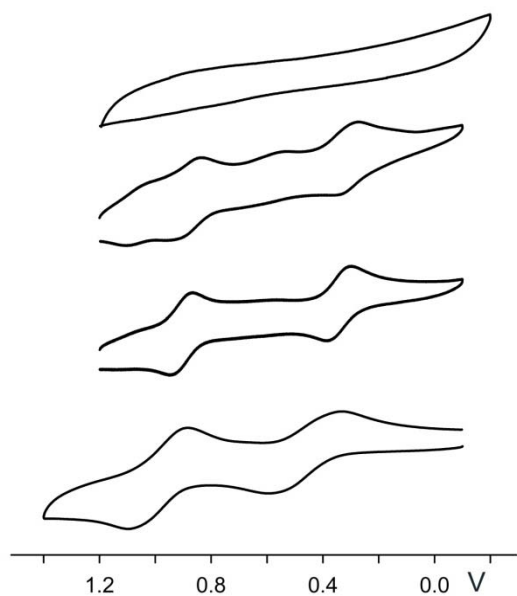


Fig S5 Change in CV of **1** (bottom) with time as reaction with H₂O take place to form the redox inactive **2** (top).

Table 1 Selected bond distances for **2**·4CH₂Cl₂.

Bond	Distances Å
Re–Re (Å)	2.2058(11), 2.2066(10)
Re–N (Å)	2.061(av)
Re1–O1	1.897(5)
Re3–O1	1.902(5)
Re2–O2	1.910(5)
Re4–O2	1.883(5)
Re–L _{ax}	2.514(6), 2.481(6) (OSO ₂ CF ₃)
(axial ligand)	2.375(6), 2.396(6) (OH)

Table 2 Crystallographic data for 2·4CH₂Cl₂.

Chemical formula	Re ₄ C ₄₆ H ₇₄ N ₁₈ O ₁₆ S ₄ F ₁₂ ·4CH ₂ Cl ₂
Fw	2575.98
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.399(8)
<i>b</i> (Å)	15.484(10)
<i>c</i> (Å)	20.484(12)
α (°)	80.220(11)
β (°)	86.058(11)
γ (°)	75.259(10)
<i>V</i> (Å ³)	4049(4)
<i>Z</i>	2
<i>d</i> _{calcd} (g·cm ⁻³)	2.113
μ (mm ⁻¹)	6.425
T (K)	213
R1 ^a (wR2 ^b)	0.0380 (0.0975)

^a R1 = $[\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$. ^b wR2 = $[\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$,
 $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$.

References

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