

Electronic Supplementary Information

Unprecedented Spin Localisation in a Metal-Metal Bonded Dirhenium Complex

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Experimental Section

Synthesis. The disodium salt of maleontrilethiolate, Na₂mnt, was prepared following the literature procedure.¹ [N(*n*-Bu)₄]₂[Re₂Cl₈] was purchased from Aldrich. Solvents either were dried with a system of drying columns from the Glass Contour Company (CH₂Cl₂, Et₂O, hexanes) or freshly distilled according to standard procedures (1,2-C₂H₄Cl₂, *t*-BuOMe).²

[N(*n*-Bu)₄]₃[Re₂(mnt)₅]. Blue-green [N(*n*-Bu)₄]₂[Re₂Cl₈] (77mg; 0.067 mmol) and pale yellow Na₂(mnt) (75mg, 0.402 mmol) were combined with dichloromethane (25 mL) in a 50 mL Schlenk flask charged with a magnetic bar under a N₂ atmosphere. The stirred reaction mixture gradually changed color from green to brownish-yellow and then dark brown. After 6 h, the reaction solution was filtered through Celite, and the solvent was subsequently removed under vacuum. The residue was washed with hexanes (3 × 5 mL) followed by diethyl ether (3 × 5 mL) and then was dried under vacuum. Yield: 39 mg (38%). Diffraction quality black needles were grown by slow diffusion of *t*-BuOMe into a 1,2-dichloroethane solution of the complex.

Anal. Calcd for C₇₀H₁₁₂Cl₂N₁₃S₁₀Re₂: C, 44.25; H, 5.94; N 9.58; S, 16.87. Found: C, 44.80; H, 5.88; N 9.93; S, 15.65%. IR (KBr, cm⁻¹): ν(CN) 2208 s, 2194 m.

The same reaction performed in an aerobic environment yielded a product identified as [N(*n*-Bu)₄]₄[ReO(mnt)₂].³

X-ray Crystallographic Data Collection and Structure Refinement. Diffraction quality crystals of [N(*n*-Bu)₄]₃[Re₂(mnt)₅]·C₂H₄Cl₂ as black needles were obtained by slow diffusion of *t*-BuOMe vapour into a 1,2-dichloroethane solution under a N₂ atmosphere. When the preparation of [N(*n*-Bu)₄]₃[Re₂(mnt)₅] was attempted in the open atmosphere, the product isolated was [N(*n*-

$\text{Bu}_4][\text{ReO}(\text{mnt})_2]$, orange block crystals of which were obtained by the diffusion of Et_2O vapor into a MeCN solution. The crystals were coated with paratone oil and mounted on the end of a nylon loop attached to the end of the goniometer. Data were collected with a Bruker SMART APEX CCD diffractometer equipped with a Kryoflex attachment supplying a nitrogen stream at 100 K. Full spheres of data were obtained by collecting three sets of 400 frames in ω ($0.5^\circ/\text{scan}$), collected at $\varphi = 0.00$, 90.00 and 180.00° followed by two sets of 800 frames in φ ($0.45^\circ/\text{scan}$) collected with ω constant at -30.00 and 210.00° . Frames times of 20 and 10 seconds/frame were used for $[\text{N}(n\text{-Bu})_4]_3[\text{Re}_2(\text{mnt})_5]\cdot\text{ClCH}_2\text{CH}_2\text{Cl}$ and $[\text{N}(n\text{-Bu})_4][\text{ReO}(\text{mnt})_2]$, respectively. Diffraction data were collected under control of one of the *APEX2*⁴ software packages. Raw data were reduced to F^2 values using the *SAINTE*⁵ software, and a global refinement of unit cell parameters was performed using ~9900 selected reflections from the full data set. Data for $[\text{N}(n\text{-Bu})_4]_3[\text{Re}_2(\text{mnt})_5]\cdot\text{C}_2\text{H}_4\text{Cl}_2$ were corrected for absorption on the basis of multiple measurements of symmetry equivalent reflections with the use of *SADABS*,⁶ while the correction for $[\text{N}(n\text{-Bu})_4][\text{ReO}(\text{mnt})_2]$ was performed analytically using the SCALE routine within *APEX2*.⁴ Structure solutions were obtained by direct or Patterson methods using *SHELXS*,⁷ while refinements were accomplished by full-matrix least-squares procedures using *SHELXL*.⁸ Both the *SHELXS* and *SHELXL* programs are incorporated into the *SHELXTL*⁹ and *APEX2* software suites.

The structure refinements were routine except that one of the *n*-butyl groups of one of the $[\text{N}(n\text{-Bu})_4]^+$ cations in $[\text{N}(n\text{-Bu})_4]_3[\text{Re}_2(\text{mnt})_5]\cdot\text{C}_2\text{H}_4\text{Cl}_2$ revealed some disorder. Three of the four carbon atoms of one *n*-butyl group were disordered over two positions and refined with a 65:35 occupancy ratio subject to restraints that imposed a geometry similar to that displayed by the other *n*-butyl groups of the cation. All hydrogen atoms were added in calculated positions ($\text{C-H} = 0.98\text{--}0.99 \text{ \AA}$) and included as riding contributions with isotropic displacement parameters tied to those of the carbon atoms to which they were attached. All images were created with the use of *XP*, which also is part of the *SHELXTL*

package.⁹ All structures were checked for overlooked symmetry and other errors by the checkCIF service provided by the International Union of Crystallography.¹⁰ Final unit cell data and refinement statistics are collected in Table S1.

Physical Methods. Cyclic voltammogrammetry and coulometric measurements were performed with an EG&G potentiostat/galvanostat. Elemental analyses were performed by Midwest Microlab, LLC of Indianapolis, IN. Electronic absorption spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer (range 200 – 1100 nm). The X-band EPR spectrum was recorded on a Bruker ELEXSYS E500 spectrometer and simulated using the simulation package XSOPHE.¹¹ The spectra were simulated using the spin-Hamiltonian:

$$\hat{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \mathbf{I} \cdot \mathbf{P} \cdot \mathbf{I}$$

$$\hat{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + P_{zz} [3I_z^2 - I(I+1)] + (P_{xx} - P_{yy})(I_x^2 - I_y^2)$$

where μ_B is the electronic Bohr magneton, B is the applied magnetic field, g and A are the electronic g matrix and $^{185,187}\text{Re}$ nuclear hyperfine matrix, respectively, and P_{ii} ($i = x, y, z$) are the principal values of the nuclear quadrupole interaction tensor P , defined by:

$$P_{ii} = \frac{eQq_{ii}}{2I(2I-1)}$$

and

$$q_{ii} = \frac{\partial^2 V}{\partial i^2}$$

where e is the electronic charge, Q is the quadrupole moment of the $^{185,187}\text{Re}$ nuclei (2.33 and $2.22 \times 10^{-24} \text{ cm}^2$, respectively) and q_{ii} are the principal values of the electric field gradient at the nucleus. The P tensor is traceless, and its principal components are parameterized by $P = [P_{zz} - (P_{xx} + P_{yy})/2]/3$ and a rhombic term, $\eta = (P_{xx} - P_{yy})/2$.

Calculations. All calculations in this work were performed with the electronic structure program ORCA.¹² Geometry optimizations were carried out using the B3LYP functional.¹³ A segmented all-electron relativistically contracted basis set of triple- ζ -quality (def2-TZVP) was used all atoms.¹⁴ A scalar relativistic correction was applied using the zeroth-order regular approximation (ZORA) method.¹⁵ In the context of ZORA, a one center approximation has been shown to introduce only minor errors to the final geometries. Auxiliary basis sets for all complexes used to expand the electron density in the calculations were chosen to match the orbital basis. The self-consistent field (SCF) calculations were tightly converged ($1 \times 10^{-8} E_h$ in energy, $1 \times 10^{-7} E_h$ in the density change, and 1×10^{-7} in the maximum element of the DIIS error vector). The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints. Single point energies were run using the same conditions detailed for the optimization. Kohn-Sham orbitals and density plots were constructed using the program Molekel.¹⁶

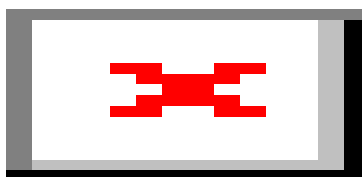


Fig. S1 Structure of the anion in crystals of $[N(n\text{-Bu})_4][\text{ReO}(\text{mnt})_2]$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Re(1)–O(1) 1.688(1), Re(1)–S(1) 2.3180(4), Re(1)–S(2) 2.3136(4), Re(1)–S(3) 2.3229(4), Re(1)–S(4) 2.3263(4).

Table S1 Crystallographic Data

compound	[N(<i>n</i> -Bu) ₄] ₃ [Re ₂ (mnt) ₅]	[N(<i>n</i> -Bu) ₄][ReO(mnt) ₂]
solvent	C ₂ H ₄ Cl ₂	none
formula	C ₇₀ H ₁₁₂ Cl ₂ N ₁₃ S ₁₀ Re ₂	C ₂₄ H ₃₆ N ₅ OS ₄ Re
fw	1899.63	725.02
<i>T</i> , K	100	100
λ , Å	0.71073	0.71073
2 θ range, deg	4.00 – 55.88	5.11 – 55.99
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	27.314(2)	11.5743(8)
<i>b</i> , Å	11.0154(7)	11.7501(8)
<i>c</i> , Å	29.688(2)	12.5007(8)
α , deg	90	86.489(1)
β , deg	104.371(1)	86.473(1)
γ , deg	90	60.987(1)
<i>V</i> , Å ³	8653(1)	1483(2)
<i>Z</i>	4	2
ρ , g cm ⁻³	1.458	1.623
μ , mm ⁻¹	3.144	4.403
crystal size	0.10 × 0.13 × 0.18	0.21 × 0.23 × 0.27
color, habit	black column	orange block
limiting indices, <i>h</i>	-35 < <i>h</i> < 35	-15 < <i>h</i> < 15
limiting indices, <i>k</i>	-14 < <i>k</i> < 14	-15 < <i>k</i> < 15
limiting indices, <i>l</i>	-39 < <i>l</i> < 39	-16 < <i>l</i> < 16
reflections collected	146858	25755
independent data	20740	7092
restraints	6	0
parameters refined	895	321
GoF ^a	1.067	1.082
R1, ^{b,c} wR2 ^{d,e}	0.0331, 0.0668	0.0142, 0.0358
R1, ^{b,e} wR2 ^{d,e}	0.0456, 0.0714	0.0145, 0.0360
largest diff. peak, e Å ⁻³	1.331	0.814
largest diff. hole, e Å ⁻³	-1.513	-0.733

^a GoF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* = number of reflections and *p* is the total number of parameters refined. ^b R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^c R indices for data cut off at $I > 2\sigma(I)$. ^d wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$. ^e R indices for all data.

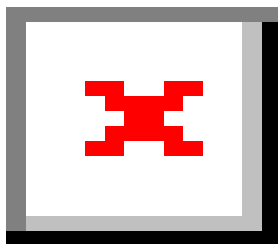


Fig. S2 Electronic spectral titration for the electrochemical reduction of $[\text{Re}_2(\text{mnt})_5]^{3-}$ (red) to $[\text{Re}_2(\text{mnt})_5]^{4-}$ (black) recorded in CH_2Cl_2 (0.10 M $[\text{N}(n\text{-Bu})_4]\text{PF}_6$) at $-25\text{ }^\circ\text{C}$.

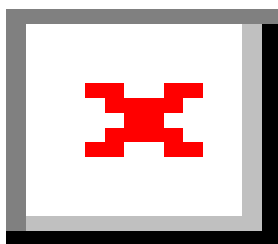


Fig. S3 Electronic spectral titration for the electrochemical oxidation of $[\text{Re}_2(\text{mnt})_5]^{3-}$ (red) to $[\text{Re}_2(\text{mnt})_5]^{2-}$ (blue) recorded in CH_2Cl_2 (0.10 M $[\text{N}(n\text{-Bu})_4]\text{PF}_6$) at $-25\text{ }^\circ\text{C}$.

Table S2 Comparison of calculated and experimental (in parentheses) metric parameters (Å)

	$[\text{Re}_2(\text{mnt})_5]^{2-}$		$[\text{Re}_2(\text{mnt})_5]^{3-}$		$[\text{Re}_2(\text{mnt})_5]^{4-}$
Re(1)–Re(2)	2.798	2.736	(2.6654(2))	2.705	
b.o. (Löwdin)	1.05	1.20	(1.28)	1.33	
Re(1)–S _{av}	2.410	2.422	(2.4030(9))	2.422	
Re(2)–S _{av}	2.389	2.395	(2.3724(9))	2.402	

Table S3 Geometry-optimised coordinates for $[\text{Re}_2(\text{mnt})_5]^{3-}$

Re	2.788343	-0.014623	0.022845
Re	0.052730	-0.010139	-0.003463
S	4.584737	-1.527025	-0.658037
S	3.076545	0.917845	-2.155402
S	4.581139	1.484662	0.739508
S	3.027620	-0.949318	2.206401
S	-1.756764	-1.646611	0.119782
S	-1.750871	1.628922	-0.166321
S	-0.175163	-0.056863	2.385682
S	1.339736	1.921537	0.311364
S	-0.126764	0.035514	-2.398497
S	1.339320	-1.945896	-0.292601
N	7.199692	-2.073259	-3.203199
N	5.312791	1.094507	-5.095582
N	7.159776	2.001508	3.328242
N	5.215586	-1.154532	5.181055
N	-5.417476	-2.061410	0.115264
N	-5.409876	2.049059	-0.250541
N	0.304830	1.933138	5.451179
N	2.239378	4.543857	2.790857
N	0.405868	-1.961622	-5.451234
N	2.273410	-4.576956	-2.750360
C	5.131455	-0.896913	-2.185313
C	4.500690	0.160121	-2.824716
C	5.097703	0.846481	2.274164
C	4.447377	-0.206525	2.900530
C	-3.219175	-0.699683	0.017430
C	-3.216974	0.683800	-0.098551
C	0.533523	1.431428	2.919701
C	1.192447	2.300859	2.066682
C	0.585010	-1.456542	-2.916294
C	1.223907	-2.327739	-2.049783
C	6.263685	-1.532674	-2.756564
C	4.957148	0.659794	-4.069286
C	6.226277	1.470460	2.865148
C	4.879530	-0.713708	4.150775
C	-4.432468	-1.430645	0.072527
C	-4.427532	1.416241	-0.183484
C	0.423551	1.717321	4.309131
C	1.764170	3.517556	2.484983
C	0.499958	-1.745816	-4.306914
C	1.796850	-3.548250	-2.454886

Table S4 Geometry-optimised coordinates for $[\text{Re}_2(\text{mnt})_5]^{2-}$

Re	2.766958	-0.011590	0.024479
Re	-0.031064	-0.006211	-0.004585
S	4.500028	-1.497056	-0.691023
S	2.975126	0.888956	-2.148870
S	4.491710	1.462282	0.780543
S	2.930036	-0.923023	2.199488
S	-1.824127	-1.610641	0.197712
S	-1.814333	1.601924	-0.249490
S	-0.177561	0.023874	2.394289
S	1.260474	1.940189	0.234853
S	-0.128684	-0.044179	-2.408217
S	1.257414	-1.958433	-0.213695
N	7.382560	-1.708264	-2.988814
N	5.476465	1.504667	-4.817454
N	7.346960	1.631802	3.116210
N	5.396830	-1.582457	4.891625
N	-5.483320	-2.052368	0.233484
N	-5.468839	2.054357	-0.381224
N	0.346169	2.121986	5.382053
N	2.208320	4.648298	2.584956
N	0.437788	-2.164389	-5.374534
N	2.234358	-4.682004	-2.533849
C	5.187164	-0.695885	-2.064142
C	4.544607	0.366868	-2.690252
C	5.155879	0.644009	2.155525
C	4.496701	-0.418410	2.764864
C	-3.291335	-0.689980	0.051170
C	-3.287432	0.684349	-0.140630
C	0.510661	1.539695	2.862959
C	1.140438	2.383207	1.964050
C	0.558807	-1.565791	-2.856654
C	1.167774	-2.408386	-1.942517
C	6.390598	-1.245371	-2.582913
C	5.066169	0.978403	-3.858657
C	6.356860	1.179616	2.693923
C	4.999705	-1.044568	3.933724
C	-4.500637	-1.424572	0.152254
C	-4.491865	1.421640	-0.273505
C	0.433046	1.870757	4.245567
C	1.720696	3.617423	2.323332
C	0.503349	-1.905215	-4.238430
C	1.747267	-3.647650	-2.285387

Table S5 Geometry-optimised coordinates for $[\text{Re}_2(\text{mnt})_5]^{4-}$

Re	2.888080	-0.014754	0.022534
Re	0.183097	-0.014675	-0.002494
S	4.719728	-1.566765	-0.553504
S	3.287670	0.851638	-2.169342
S	4.711969	1.532159	0.636238
S	3.243180	-0.884126	2.221797
S	-1.640179	-1.673103	-0.046253
S	-1.639935	1.645379	0.003860
S	-0.115146	-0.262809	2.364847
S	1.473952	1.878192	0.480433
S	-0.069583	0.234164	-2.375093
S	1.481870	-1.907733	-0.461254
N	6.883675	-2.739227	-3.311303
N	4.996409	0.306559	-5.408488
N	6.835882	2.685548	3.434152
N	4.902471	-0.361420	5.488168
N	-5.301411	-2.068274	-0.100909
N	-5.304319	2.037205	-0.024164
N	0.269212	1.480431	5.589232
N	2.202153	4.338118	3.188278
N	0.387265	-1.494055	-5.594872
N	2.245245	-4.375658	-3.151971
C	5.051143	-1.258389	-2.243393
C	4.429234	-0.233712	-2.944420
C	5.014450	1.217294	2.330647
C	4.376641	0.193357	3.018074
C	-3.099590	-0.709257	-0.052502
C	-3.099499	0.682155	-0.022726
C	0.586247	1.178748	3.035908
C	1.252368	2.123297	2.273382
C	0.643529	-1.207757	-3.032858
C	1.292786	-2.153757	-2.257755
C	6.050396	-2.059072	-2.845978
C	4.754564	0.048688	-4.290875
C	6.007555	2.010712	2.952431
C	4.678192	-0.094563	4.368995
C	-4.314911	-1.435581	-0.078207
C	-4.315170	1.408291	-0.024419
C	0.434434	1.351384	4.438306
C	1.770411	3.317706	2.800605
C	0.519242	-1.379167	-4.438160
C	1.818412	-3.349312	-2.774731

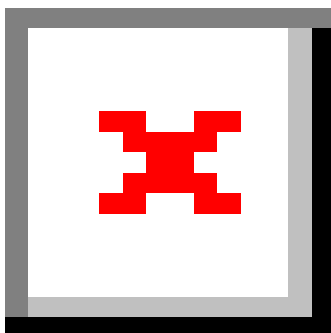


Fig. S4 Geometry-optimised structure of [Re₂(mnt)₅]³⁻

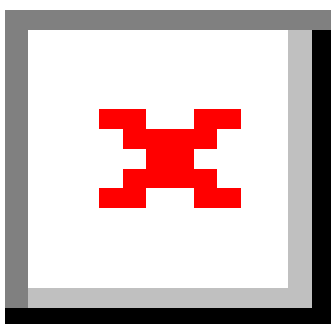


Fig. S5 Geometry-optimised structure of [Re₂(mnt)₅]²⁻

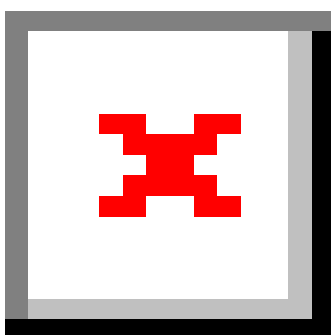


Fig. S6 Geometry-optimised structure of [Re₂(mnt)₅]⁴⁻

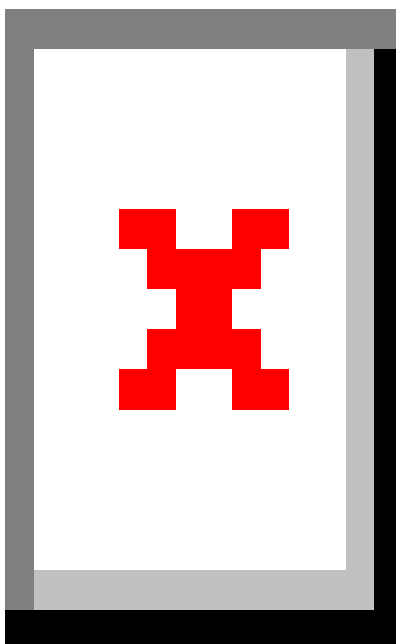


Fig. S7 Qualitative MO scheme depicting the ordering of the frontier orbitals (β -spin) for the $\{\text{Re}_2\}^{8+}$ unit in $[\text{Re}_2(\text{mnt})_5]^{2-}$.

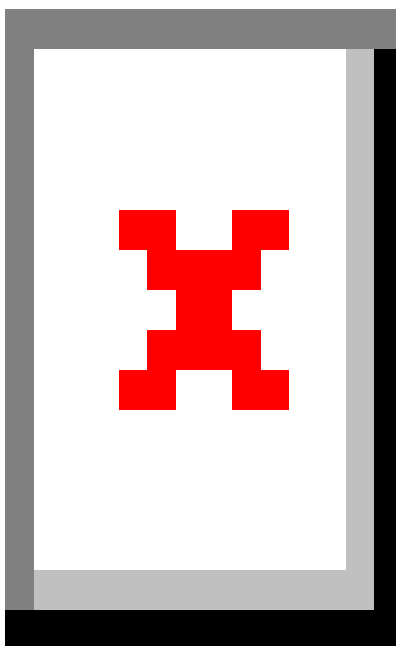


Fig. S8 Qualitative MO scheme depicting the ordering of the frontier orbitals (β -spin) for the $\{\text{Re}_2\}^{6+}$ unit in $[\text{Re}_2(\text{mnt})_5]^{4-}$.

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