SUPPLEMENTARY MATERIALS

Novel mononuclear tetrabromonitrosylrhenate(II) complexes containing azole-type ligands: magnetostructural characterization through Hirshfeld surfaces analysis

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Table S1. List of the infrared absorption bands observed in compounds **1**-**4**, and classified upon their origin. (ligand, NBu_4^+ or Re-NO).

Compound	Ligand (L)	NBu_4^+	Re-NO	Ref
1	3150(w), 3144(w), 1481(m), 1378(m), 1356(w), 1306(w), 1283(w), 1145(m), 1043 (m), 997(m), 888(m) and 675(m)	2962(m), 2923(m), 2873(m) and 1470(m)	1765(s)	[24]
2	457(m), 1355(m), 1152(w), 1135(s), 1135(s), 773(s), 665(m), and 619(w)	2960(s), 2932(m), 2872(m), 1408(m), 1378(w), 1065(m), 1027(w), and 737(m)	1769(s)	[25]
3	3150(w), 3144(w), 1481(m), 1378(m), 1356(w), 1306(w), 1283(w), 1145(m), 1043(m), 997(m), 888(m) y 675(m)	2960(m), 2933 (w), 2871 (m), 1470 (m), and 738 (w)	1769(s)	[24]
4	3159(m), 1255(w), 1126(m), 1063(w), 1030(w), 881(w), 658(m)	2963(m), 2876(w), 1467(m) and 881(w)	1765(s)	[26]

Table S2. Summary of the crystal data and structure refinement for **1**-**4**.[a]

Compound	1	2	3	4
Empirical formula	$C_{19}H_{40}Br_4N_4ORe$	$C_{19}H_{40}Br_4N_4ORe$	$C_{18}H_{39}Br_4N_5ORe$	$C_{34}H_{76}Br_8N_{12}O_2Re_2$
Formula weight	846.39	846.39	847.38	1695.74
T/K	150.01(10)	293(2)	149.99(10)	293(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a /Å	12.5362(4)	12.621(2)	12.5889(2)	24.5488(13)
b /Å	12.9887(4)	12.784(2)	12.8366(2)	11.3909(4)

c /Å	17.3319(8)	18.410(4)	17.3631(5)	22.8263(13)
α /°	90	90	90	90
β /°	98.597(4)	99.546(5)	98.6314(19)	115.424(7)
γ /°	90	90	90	90
Volume /Å^3	2790.44(18)	2929.3(10)	2774.06(10)	5764.8(6)
Z	4	4	4	4
ρ_{calcd}/g cm^{-3}	2.015	1.919	2.029	1.954
Absorption coefficient./mm^{-1}	10.099	9.621	10.160	9.779
F(000)	1620	1620	1620	3236
Crystal size /mm^3	0.081 x 0.06 x 0.031	0.305 x 0.168 x 0.077	0.286 x 0.152 x 0.08	0.126 x 0.091 x 0.032
θ range for data collection/°	1.878 to 28.238	3.006 to 26.872	1.871 to 28.310	1.786 to 28.425
Index ranges	-8 ≤ *h* ≤ 16 -17 ≤ *k* ≤ 16 -22 ≤ *l* ≤ 22	-16 ≤ *h* ≤ 16 -16 ≤ *k* ≤ 16 -23 ≤ *l* ≤ 23	-15 ≤ *h* ≤ 10 -14 ≤ *k* ≤ 16 -20 ≤ *l* ≤ 21	-32 ≤ *h* ≤ 32 -14 ≤ *k* ≤ 11 -23 ≤ *l* ≤ 30
Reflect. collected	21285	86900	11248	24758
Independent reflect. [*R*(int)]	6336 [0.0499]	6293 [0.0601]	6188 [0.0221]	12670 [0.0544]
Completeness to θ = 25.242 (**1, 3** and **4**) or 26.000° (**2**)	100.00%	99.80%	100.00%	99.4%
Absorption correction	Gaussian	Semi-empirical from equivalents	Gaussian	Gaussian
Max./min. transmission	0.774/0.591	0.745/0.532	0.473/0.143	0.836/0.443
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data/restraints / parameters	6336/0/ 266	6293/0/264	6188/0/252	12670/135/531
[a]Goodness-of-fit on F^2	0.975	1.040	1.047	1.204
[b]R_1 [$I > 2\sigma(I)$]	0.0337	0.0264	0.0299	0.0673
[b]*wR*2 (all data)	0.0459	0.0495	0.0588	0.1768
Extinction coefficient	n/a	n/a	n/a	n/a
Largest diff. peak and hole/e Å^{-3}	0.890 and -1.164	0.538 and -0.670	1.384 and -0.972	1.418 and -0.904

[a]Goodness-of-fit: $S = \sqrt{\frac{\sum\left[w\left(F_o^2 - F_c^2\right)^2\right]}{(N-P)}}$. [b] $R = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$ and $wR2 = \sqrt{\frac{\sum[w(F_o^2-F_c^2)^2]}{\sum[w(F_o^2)^2]}}$

Table S3. Geometrical distortion from OC-6 calculated by CSM (OC-6) and the calculated tetragonal distortion for several tetrabromonitrosylrhenium(II) complexes.

L =	OC-6	dist (Re-N) / Å	$\nu = \Delta/\lambda\kappa$	Ref
Pirazole	1.397	2.191	-2.28	This work
Imidazole	1.460	2.173	-1.94	This work
1,2,4-triazole	1.369	2.194	-1.55	This work
1H-Tetrazole	1.269	2.182	-1.70	This work
Pyridine	1.300	2.218	-2.30	9
3-Pyiridinecarboxylic acid	1.266	2.225	-1.88	10
3,5-Pyridinedicarboxylic acid	1.075	2.230	-1.57	11
Pyrazine	1.454	2.215	-1.52	9
pyrimidine	1.291	2.227	-1.68	9
pyridazine	1.275	2.234	-1.85	9

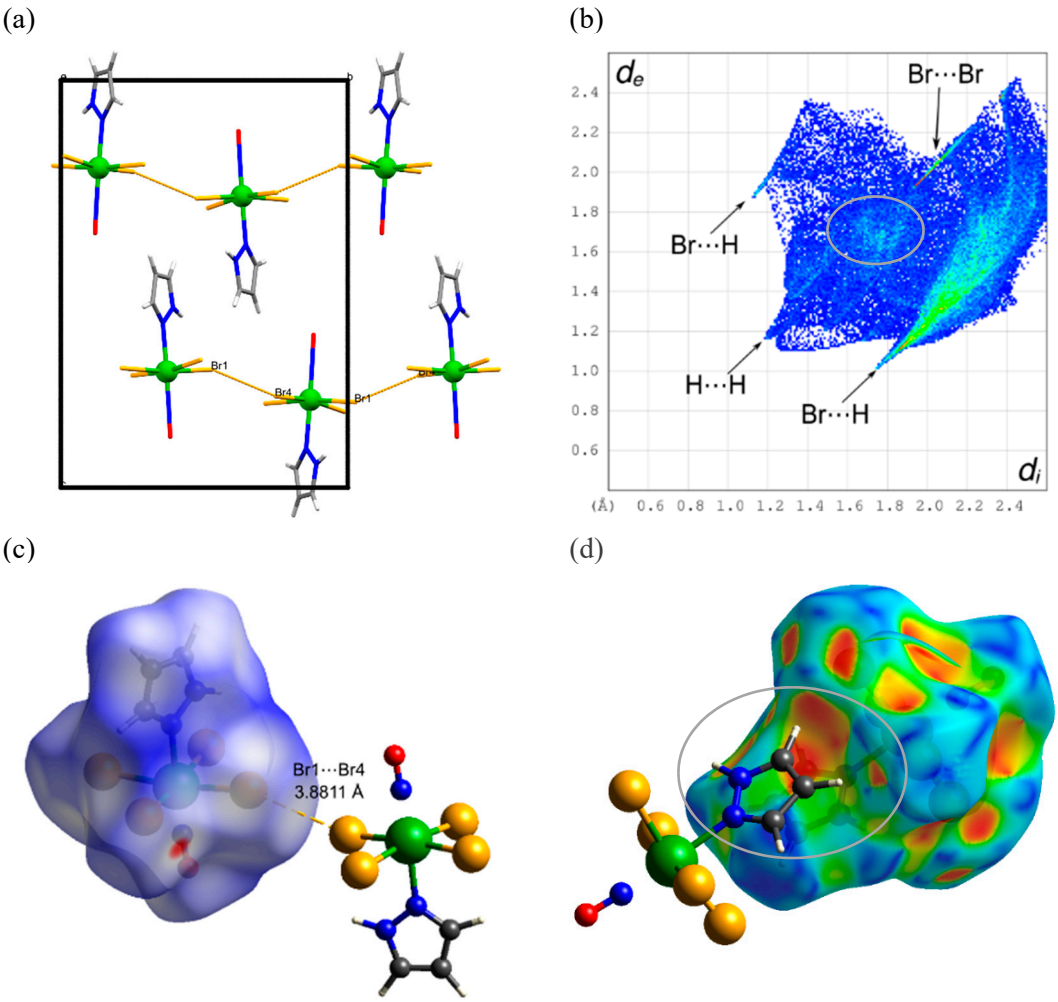

Figure S1. (a) Packing diagram down the crystallographic *a* axis, (b) fingerprint plot, (c) d_{norm} surface, and (d) shape index surface of the $[Re(NO)Br_4(Hpz)]^-$ anionic units in **2**. Short Br···Br (yellow dashed lines) contacts and π-π stacking interactions (grey ovals) are shown.

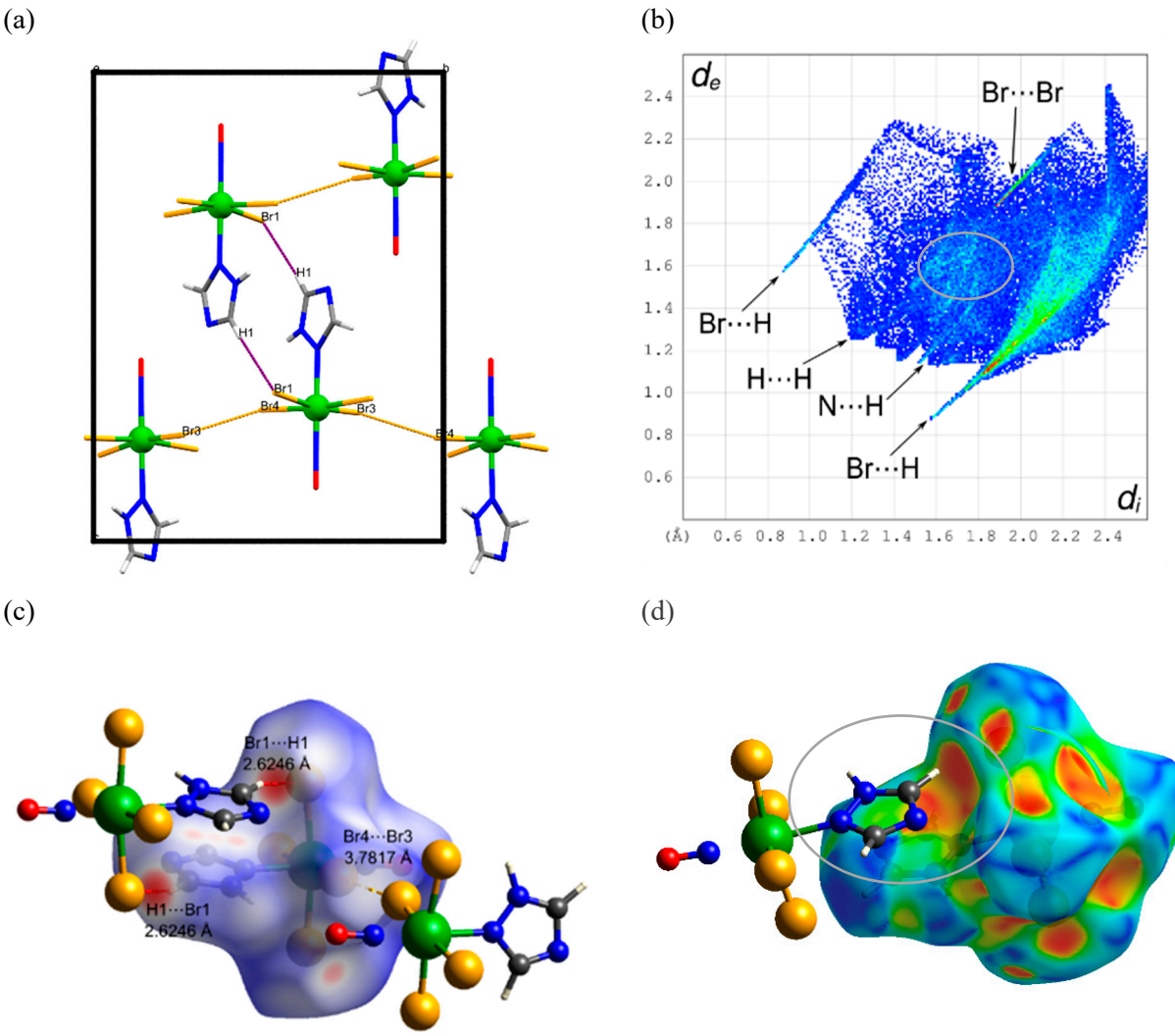

Figure S2. (a) Packing diagram down the crystallographic *a* axis, (b) fingerprint plot, (c) d_{norm} surface, and (d) shape index surface of the $[Re(NO)Br_4(Htz)]^-$ anionic units in **3**. Short Br···Br (yellow), Br···H (red) contacts and π-π stacking interactions (grey ovals) are shown.

References

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