Supplementary Information

Magneto-structural correlations in dirhenium(IV) complexes possessing magnetic pathways with even or odd numbers of atoms.

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	1	**2**	**3**	**4**
Crystal data				
Chemical formula	$C_4H_4Cl_{10}N_2Re_2\cdot2(C_{16}H_{36}N)$	$C_4H_4Br_{10}N_2Re_2\cdot2(C_{16}H_{36}N)$	$C_4H_4Br_{10}N_2Re_2\cdot2(C_{16}H_{36}N)$	$C_3H_3Br_{10}N_3Re_2\cdot2(C_{16}H_{36}N)$
M_r	1291.96	1736.50	1736.50	1737.50
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1$	Monoclinic, $I2/a$
Temperature (K)	295	120	293	120
a, b, c (Å)	15.6173(3), 19.3882(4), 16.8316(4)	11.0630 (3), 22.3446 (5), 11.9834 (4)	16.5547 (3), 15.1382 (2), 21.5926 (3)	23.7287 (5), 11.12035 (19), 20.8616 (5)
β (°)	91.5337(19)	115.626 (4)	90.122 (2)	108.371 (2)
V (Å^3)	5094.63(18)	2670.90 (14)	5411.27 (14)	5224.26 (19)
Z	4	2	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	5.301	12.04	11.88	12.31
Crystal size (mm)	0.17×0.09×0.05	0.35×0.19×0.07	0.70×0.11×0.04	0.21×0.11×0.08
Data collection				
T_{min}, T_{max}	0.977, 0.992	0.755, 0.923	0.318, 0.938	0.832, 0.926
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	130073, 18129, 14396	56629, 8154, 6199	94121, 25646, 18840	66891, 7965, 7101
R_{int}	0.079	0.069	0.067	0.051
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	×	0.728	0.686	0.726
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040,0.058,1.06	0.042, 0.080, 1.05	0.045, 0.077, 0.96	0.028, 0.045, 1.12
No. of reflections	18129	8154	25646	7965
No. of parameters	477	287	973	240
No. of restraints	0	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.83, -1.14	2.09, −2.91	1.41, −1.22	1.10, −1.56

Table S1. Crystallographic parameters for **1**-**4**.

Structure	**1** (X; Cl)	**2** (X; Br)
Bond lengths / Å		
Re–X	2.3006(8)–2.3552(8)	2.4489(6)–2.4953(6)
Re–N / Å	2.180(2), 2.175(2)	2.196(4)
Bond angles / °		
X_{eq}–Re–X_{eq}	88.71(3)–91.08(3)	89.042(19)– 90.63(2)
X_{trans}–Re–N	178.55(7), 179.18(7)	178.57(11)
Out-of-plane / Å		
Re–X_{eq} plane	0.1186(4), 0.1207(4)	0.1148(4)
	3	**4**
Bond lengths / Å		
Re–Br	2.4476(14)–2.5185(14)	2.4495(3)–2.5009(3)
Re–N / Å	2.197(10)–2.221(10)	2.211(2)
Bond angles / °		
Br_{eq}–Re–Br_{eq}	87.64(5)–91.83(5)	89.732(11)–89.919(10)
Br_{trans}–Re–N	177.5(2)	177.52(6)
Out-of-plane / Å		
Re–Br_{eq} plane	0.1194(9)–0.1300(9)	0.1306(2)

Table S2. Structural parameters for the Re^{IV} ions in **1-4**.

	Intramolecular X···X / Å	Intermolecular X···X / Å
1, (X; Cl)	6.8602(11)	4.6976(11)
2, (X; Br)	6.9116(8)	3.5202(9)
3, (X; Br)	4.006(2)	4.707(2)
4, (X; Br)	4.5249(4)	3.4304(4)

Table S3. Shortest intra- and intermolecular halide···halide interactions in **1**-**4**.

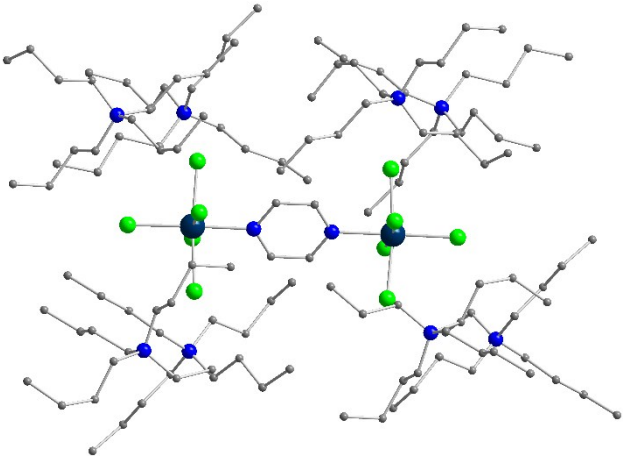

Figure S1. The packing of cations and anion in **1**. Colour code: Re = cyan, Cl = green, N = blue, C = grey. H-atoms omitted for clarity.

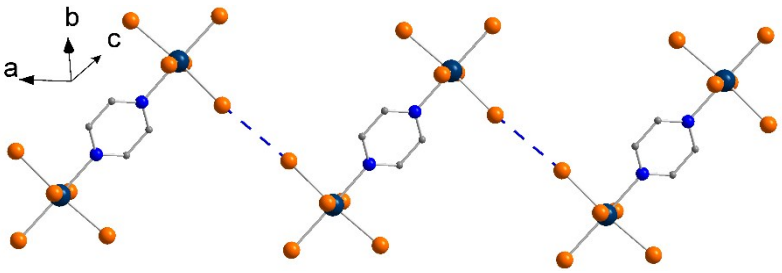

Figure S2. The 1D anionic motif of **2**. Short Br···Br distance indicated by dashed blue lines. Colour code: Re = cyan, Br = orange, N = blue, C = grey. H-atoms omitted for clarity.

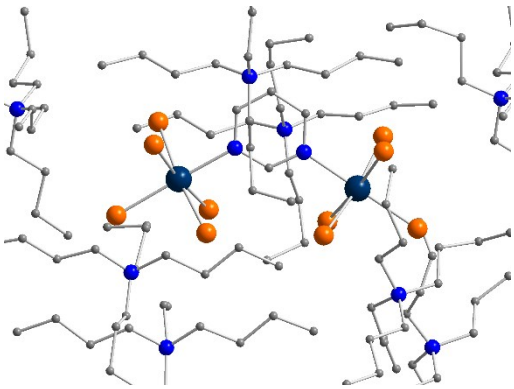

Figure S3. The anion of **3** encapsulated by the NBu4+ cations. Colour code as in Figure S2. Hydrogen atoms are omitted for clarity.

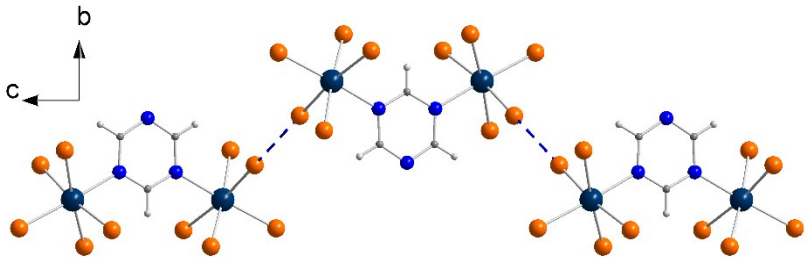

Figure S4. The Br···Br interactions in the crystal lattice of **4**. Short Br···Br distances indicated by dashed blue lines. Colour code as in Figure S2.