Electronic Supplementary Information

Magneto-structural correlations in a family of $Re^{IV}Cu^{II}$ chains based on the hexachlororhenate(IV) metalloligand

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Table S1. Crystallographic parameters for **1**-**3**.

	1	**2**	**3**
Crystal data			
Chemical formula	$Cl_6Re{\cdot}2(C_6H_8Cu_{0.5}N_4){\cdot}2(C_3H_8O)$	$Cl_6Re{\cdot}C_{16}H_{24}CuN_8$	$Cl_6Re{\cdot}C_{20}H_{24}CuN_8$
M_r	854.95	790.87	838.91
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
Temperature (K)	293	120	120
a,	10.1219 (2),	8.7712 (3),	12.69636 (15),
b,	11.0652 (3),	10.3822 (4),	14.46868 (15),
c (Å)	14.7016 (4)	21.7896 (6)	16.11703 (16)
α,	76.032 (2),	79.571 (3),	90,
β,	80.918 (2),	84.553 (2),	101.4205 (11),
γ (°)	69.748 (2)	75.646 (3)	90
V (Å^3)	1494.13 (7)	1887.95 (11)	2902.07 (6)
Z	2	3	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	5.33	6.31	5.48
Crystal size (mm)	0.19 × 0.14 × 0.07	0.21 × 0.11 × 0.05	0.11 × 0.10 × 0.08
Data collection			
T_{min}, T_{max}	0.998, 0.999	0.991, 0.997	0.860, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	48213, 8950, 8533	40420, 11033, 8605	60620, 4403, 3787
R_{int}	0.035	0.062	0.051
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.729	0.729	0.721
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.037, 1.08	0.038, 0.069, 1.06	0.027, 0.044, 1.14
No. of reflections	8950	11033	4403
No. of parameters	359	442	185
No. of restraints	1	0	3
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.86	2.20, −1.57	0.58, −0.83

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Table S2. Crystallographic parameters for **4**-**6**.

	4	**5**	**6**
Crystal data			
Chemical formula	$Cl_6Re{\cdot}C_{28}H_{48}CuN_8$	$Cl_6Re{\cdot}C_{16}H_{20}CuN_{12}$	$Cl_6Re{\cdot}C_{12}H_{28}CuN_4O_4{\cdot}C_2H_3N$
M_r	959.18	842.88	795.88
Crystal system, space group	Orthorhombic, *Pccn*	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	293	120	120
a,	19.3832 (2),	9.46035 (13),	8.46428 (19),
b,	18.6574 (2),	14.5535 (2),	8.5772 (2),
c (Å)	10.60318 (13)	9.73308 (13)	9.7582 (2)
α,	90,	90,	95.043 (2),
β,	90,	95.2788 (12),	91.8824 (19),
γ (°)	90	90	90.111 (2)
V (Å^3)	3834.54 (8)	1334.38 (3)	705.31 (3)
Z	4	2	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	4.16	5.96	5.64
Crystal size (mm)	0.87 × 0.22 × 0.14	0.37 × 0.11 × 0.08 × 0.30 (radius)	0.26 × 0.16 × 0.14
Data collection			
T_{min}, T_{max}	0.461, 1.000	0.715, 0.918	0.806, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	94317, 6774, 5771	33934, 4810, 4275	19023, 4179, 4133
R_{int}	0.040	0.034	0.030
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.759	0.765	0.729
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.093, 1.33	0.022, 0.039, 1.15	0.020, 0.048, 1.07
No. of reflections	6774	4810	4179
No. of parameters	232	166	162
No. of restraints	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.17, −0.79	0.55, −0.60	2.81, −0.63

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Table S3. Selected bond lengths and angles for **1** and **2**.

Compound	**1**		**2**
Re(1)–Cl(1) / Å	2.3481(4)	Re(1)–Cl(1) / Å	2.3695(10)
Re(1)–Cl(2) / Å	2.3803(4)	Re(1)–Cl(2) / Å	2.3670(10)
Re(1)–Cl(3) / Å	2.3437(4)	Re(1)–Cl(3) / Å	2.3512(9)
Re(1)–Cl(4) / Å	2.3597(4)	Re(2)–Cl(4) / Å	2.3469(10)
Re(1)–Cl(5) / Å	2.3536(5)	Re(2)–Cl(5) / Å	2.3617(11)
Re(1)–Cl(6) / Å	2.3614(4)	Re(2)–Cl(6) / Å	2.3681(10)
		Re(2)–Cl(7) / Å	2.3639(10)
		Re(2)–Cl(8) / Å	2.3578(11)
		Re(2)–Cl(9) / Å	2.3829(10)
Cu(1)–Cl(1) / Å	2.9929(4)	Cu(1)–Cl(1) / Å	3.0449(11)
Cu(2)–Cl(2) / Å	3.0582(4)	Cu(2)–Cl(6) / Å	3.1948(12)
		Cu(2)–Cl(9) / Å	3.0379(12)
Cu(1)–N(1) / Å	2.0026(15)	Cu(1)–N(1) / Å	1.994(3)
Cu(1)–N(3) / Å	1.9931(15)	Cu(1)–N(2) / Å	2.001(3)
Cu(1)–N(5) / Å	1.9912(15)	Cu(2)–N(5) / Å	1.998(3)
Cu(1)–N(7) / Å	1.9928(15)	Cu(2)–N(6) / Å	1.978(3)
		Cu(2)–N(7) / Å	2.001(3)
		Cu(2)–N(8) / Å	1.979(3)
cis Cl–Re–Cl / °	88.382(16)-91.617(15)	*cis* Cl–Re(1)–Cl / °	89.34(4)-90.66(4)
Cl(1)–Re(1)–Cl(2) / °	176.798(16)	*cis* Cl–Re(2)–Cl / °	88.09(4)-92.93(4)
Cl(3)–Re(1)–Cl(5) / °	178.038(18)	Cl(4)–Re(2)–Cl(7) / °	177.26(4)
Cl(4)–Re(1)–Cl(6) / °	179.713(16)	Cl(5)–Re(2)–Cl(8) / °	178.30(4)
		Cl(6)–Re(2)–Cl(9) / °	176.97(4)
Re(1)···Cu(1) / Å	5.19330(14)	Re(1)···Cu(1) / Å	5.19109(18)
Re(1)···Cu(2) / Å	5.23858(16)	Re(2)···Cu(2) / Å	5.2909(6)[a]
		Re(2)···Cu(2) / Å	5.0993(6)[b]
Re(1)–Cl(1)–Cu(1) / °	152.79(2)	Re(1)–Cl(1)–Cu(1) / °	146.71(5)
Re(1)–Cl(2)–Cu(2) / °	148.59(2)	Re(2)–Cl(6)–Cu(2) / °	143.60(4)
		Re(2)–Cl(9)–Cu(2) / °	140.03(4)

[a]intermolecular distance across the Cl(6) atom. [b]intermolecular distance across the Cl(9) atom.

Table S4. Selected bond lengths and angles for **3**-**6**.

Compound	**3**	**4**
Re(1)–Cl(1) / Å	2.3597(6)	2.3695(9)
Re(1)–Cl(2) / Å	2.3546(6)	2.3588(9)
Re(1)–Cl(3) / Å	2.3538(6)	2.3611(9)
Cu(1)–Cl(1) / Å	2.8831(6)	3.2256(10)
Cu(1)–N / Å	2.017(2)	1.987(3)
Cu(1)–N / Å	2.003(2)	1.996(3)
Re(1)···Cu(1) / Å	4.81236(4)	5.30159(7)
Cl(1)–Re(1)–Cl(2) / °	90.48(2)	90.85(4)
Cl(1)–Re(1)–Cl(3) / °	89.90(2)	89.92(3)
Cl(2)–Re(1)–Cl(3) / °	89.29(3)	89.82(4)
Re(1)–Cl(1)–Cu(1) / °	132.99(3)	142.25(4)

Compound	**5**	**6**
Re(1)–Cl(1) / Å	2.3859(4)	2.3643(5)
Re(1)–Cl(2) / Å	2.3474(4)	2.3577(5)
Re(1)–Cl(3) / Å	2.3457(5)	2.3527(5)
Cu(1)–Cl(1) / Å	2.8574(4)	2.7800(6)
Cu(1)–X / Å	2.0130(15) (X = N(1))	1.9609(16) (X = O(1))
Cu(1)–X / Å	2.0025(16) (X = N(4))	1.9450(16) (X = O(2))
Re(1)···Cu(1) / Å	4.73017(6)	4.87908(12)
Cl(1)–Re(1)–Cl(2) / °	89.090(16)	90.995(17)
Cl(1)–Re(1)–Cl(3) / °	90.014(16)	89.599(19)
Cl(2)–Re(1)–Cl(3) / °	90.205(19)	89.71(2)
Re(1)–Cl(1)–Cu(1) / °	128.659(18)	142.92(3)

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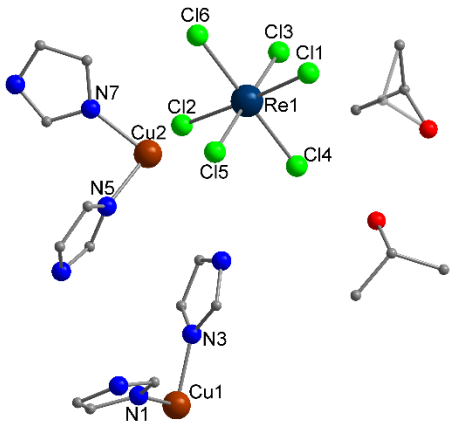

Figure S1. The asymmetric unit of **1**. Hydrogen atoms are omitted for clarity. Disorder of the isopropanol molecule is illustrated with the carbon atom at 40% transparency. Colour code: Re, cyan; Cu, brown; Cl, green; O, red; N, blue; C, grey.

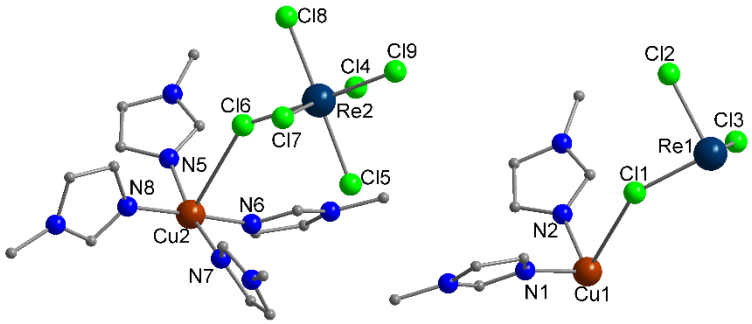

Figure S2. The asymmetric unit of **2**. Colour code as in Figure S1.

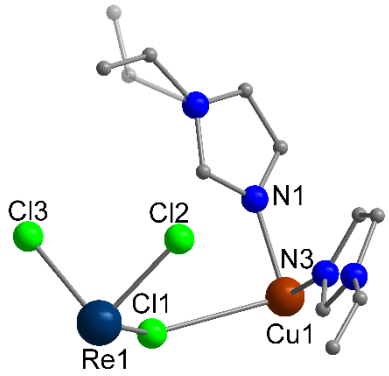

Figure S3. The asymmetric unit of **3**. Disorder of the vinyl-group is illustrated with the carbon atoms at 40% transparency. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

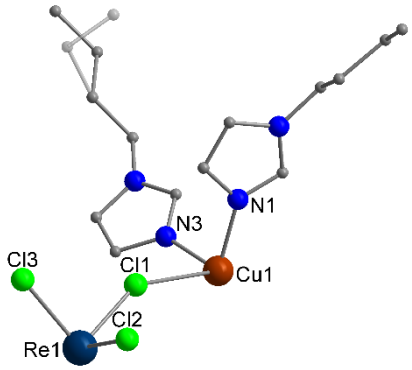

Figure S4. The asymmetric unit of **4**. Disorder of the butyl-group is illustrated with the carbon atoms at 40 % transparency. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

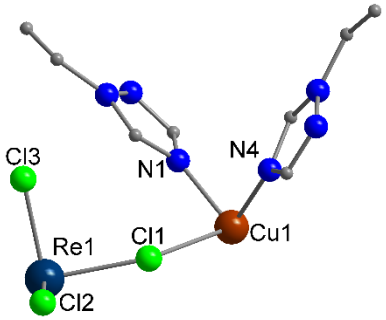

Figure S5. The asymmetric unit of **5**. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

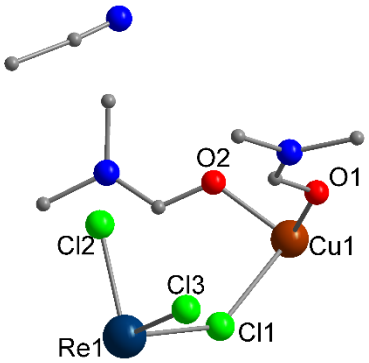

Figure S6. The asymmetric unit of **6**. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

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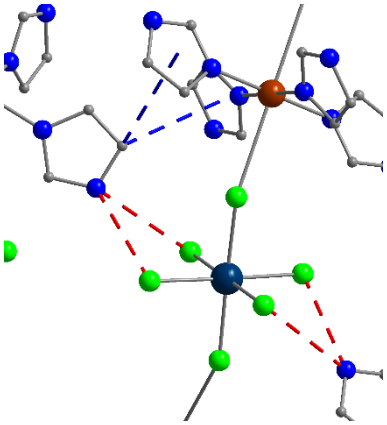

Figure S7. The intermolecular C(H)···π and N(H)···Cl interactions, blue and red dashed lines, respectively. Hydrogen atoms and isopropanol molecules omitted for clarity. Colour code as in Figure S1.

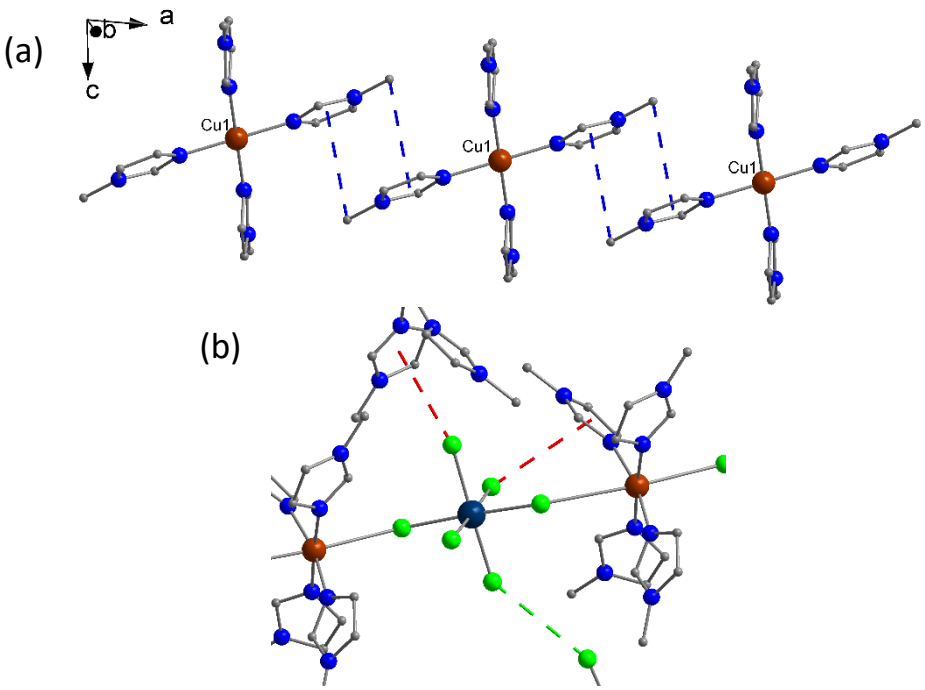

Figure S8. a) The C(H)···π interactions between the $[Cu(1)(Meim)_4]^{2+}$ cations. b) The intra- and interchain interactions of the $[ReCl_6]^{2-}$ anion. Cl···π (red), Cl···Cl (green) and CH···π (blue) interactions are indicated by dashed lines. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

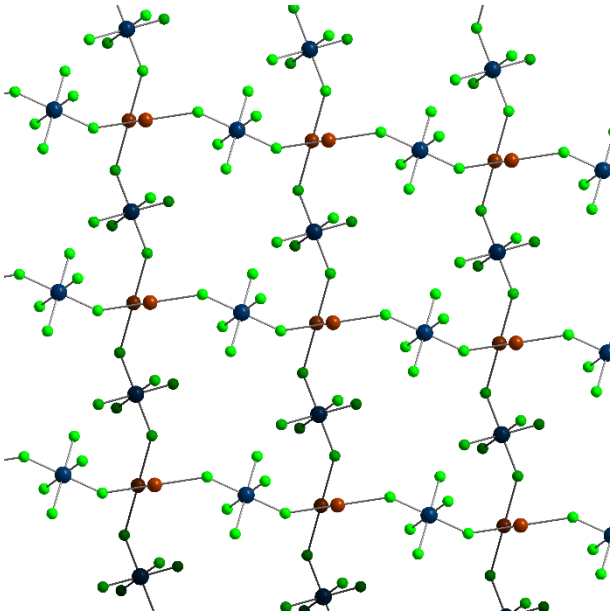

Figure S9. The packing of **3**, illustrating the two orientations of the chains. Carbon, hydrogen and nitrogen atoms omitted for clarity. Colour code as in Figure S1.

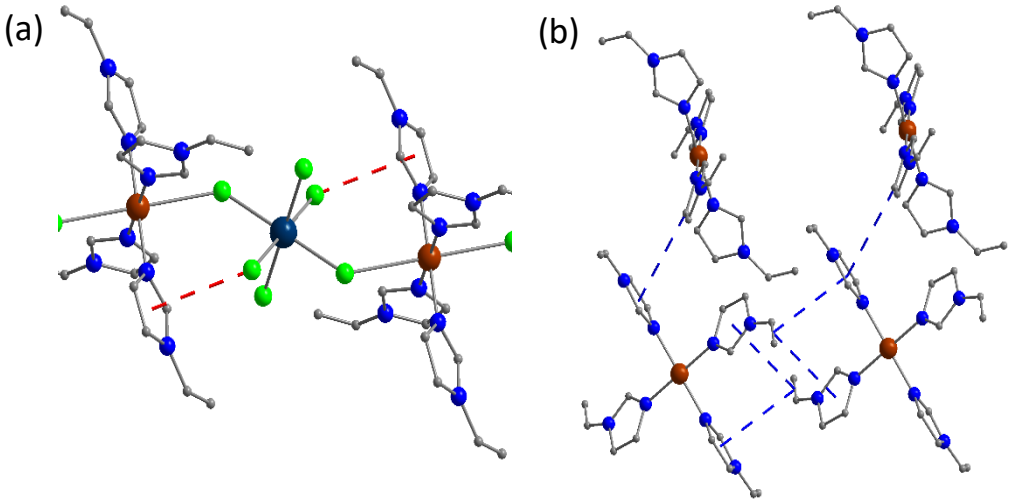

Figure S10. a) Intra-chain Cl···π interactions in **3**. b) The C(H)···π interactions between cations in **3**. Cl···π and C(H)···π interactions are represented by red and blue dashed lines, respectively. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

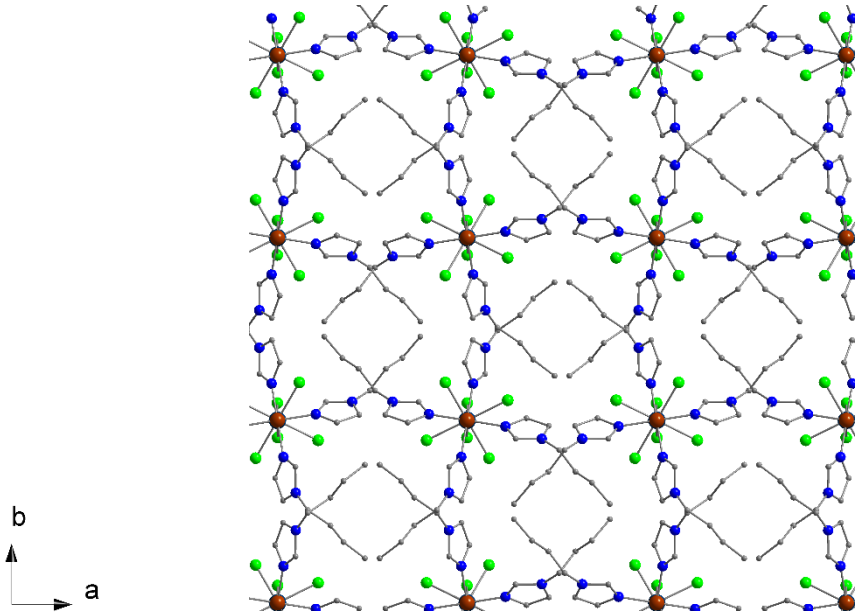

Figure S11. The packing of **4** viewed down the crystallographic *c* axis. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

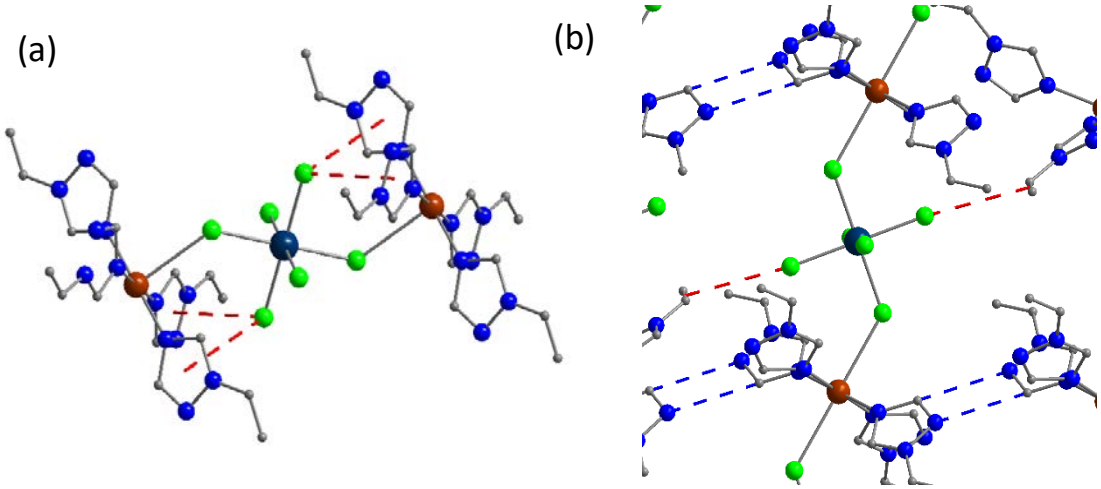

Figure S12. A view of the extended structure in **5**, showing a) intra-chain Cl···π interactions, and b) inter-chain Cl···π and C(H)···N interactions. Cl···π and C(H)···N interactions are indicated by red and blue dashed lines, respectively. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

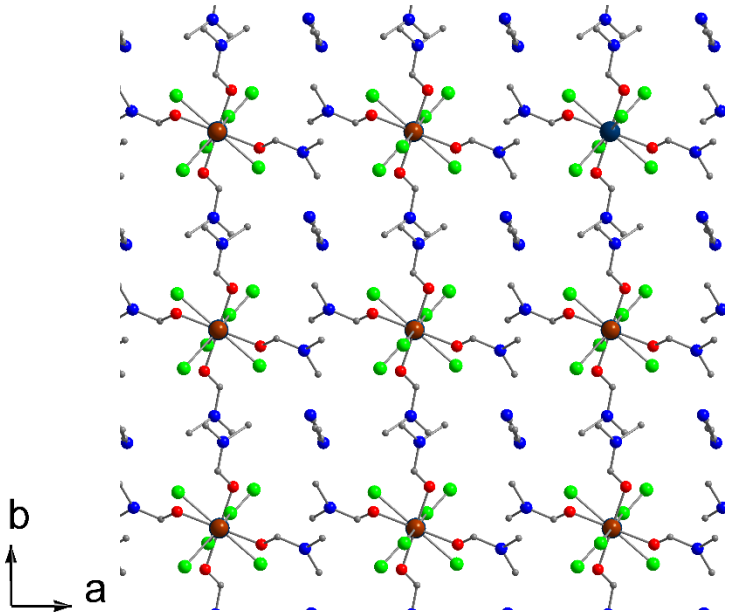

Figure S13. The packing of **6** viewed down the crystallographic *c* axis. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

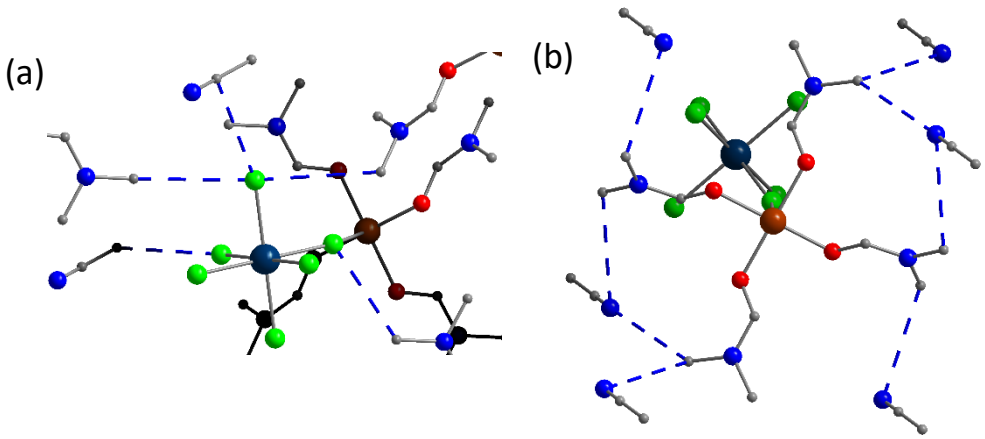

Figure S14. a) The intermolecular C(H)···Cl interactions. b) The C(H)···N interactions between DMF ligands and CH_3CN molecules. Hydrogen atoms omitted for clarity. Colour code as in Figure S1.

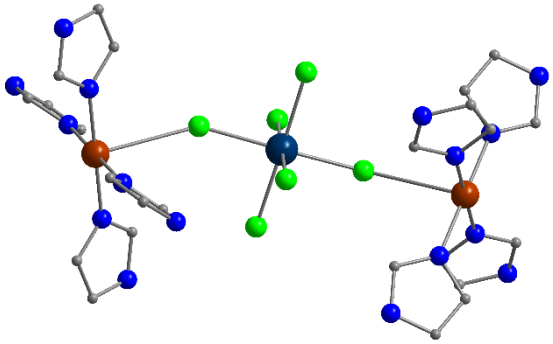

Figure S15. The $ReCu_2$ fragment, here exemplified for **1**. Colour code as Figure S1.

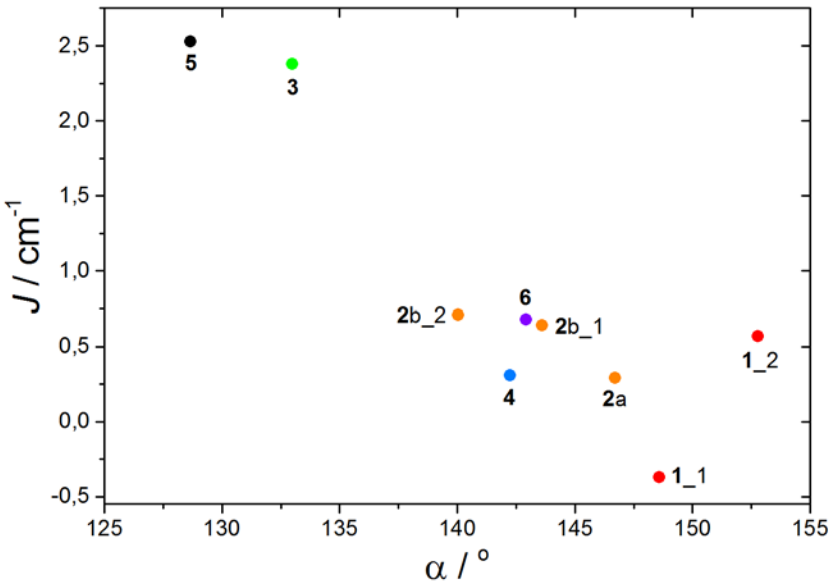

Figure S16. The magnetic exchange parameters, *J*, *versus* Re–Cl–Cu bridging angle, α. Each point labelled in accordance with Table 2.

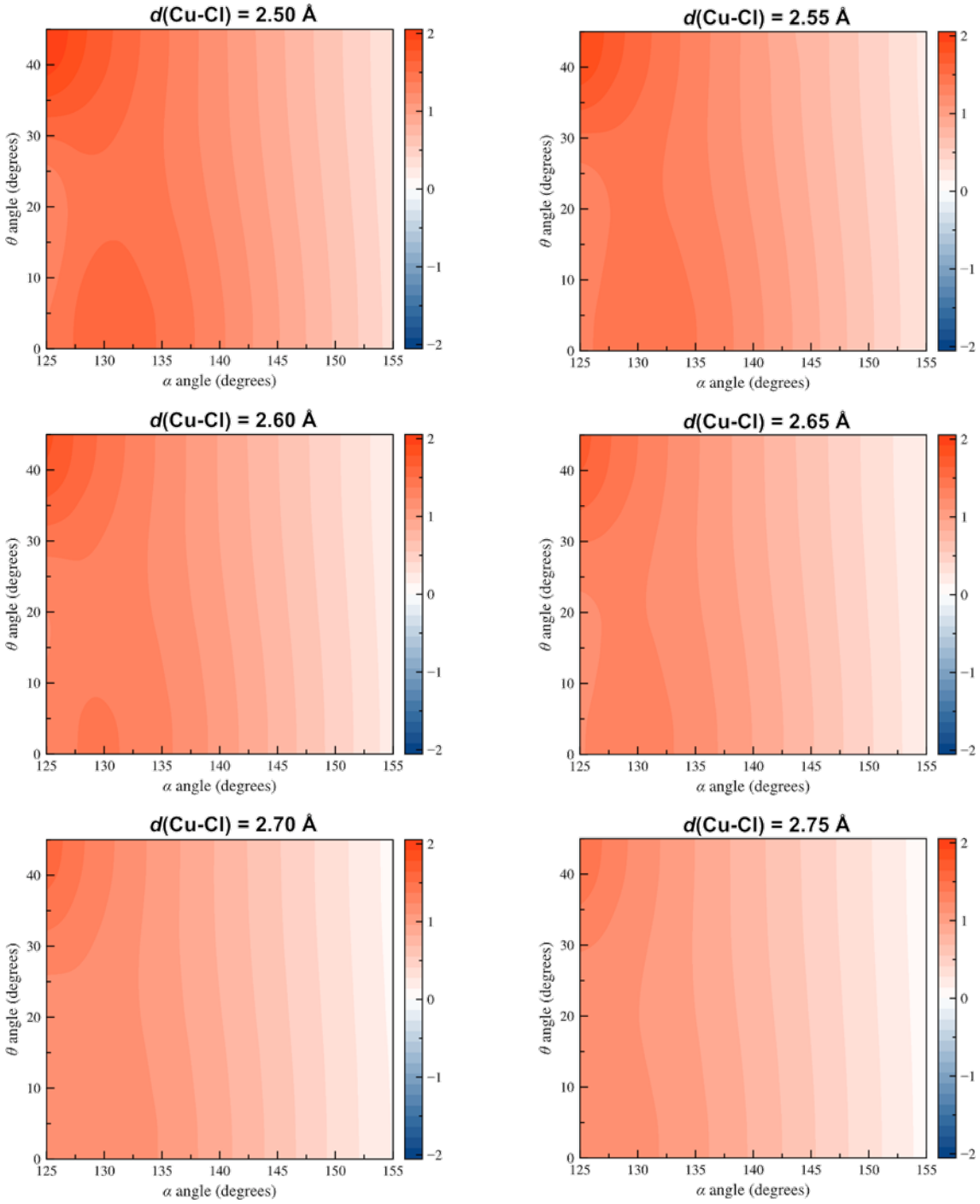

Figure S17. Contour maps of the dependence of the α and θ angles on the magnetic coupling constant in the molecular model of Fig. 4 for several Cu-Cl bond lengths in the range 2.50-2.75 Å at regular intervals of 0.05 Å.

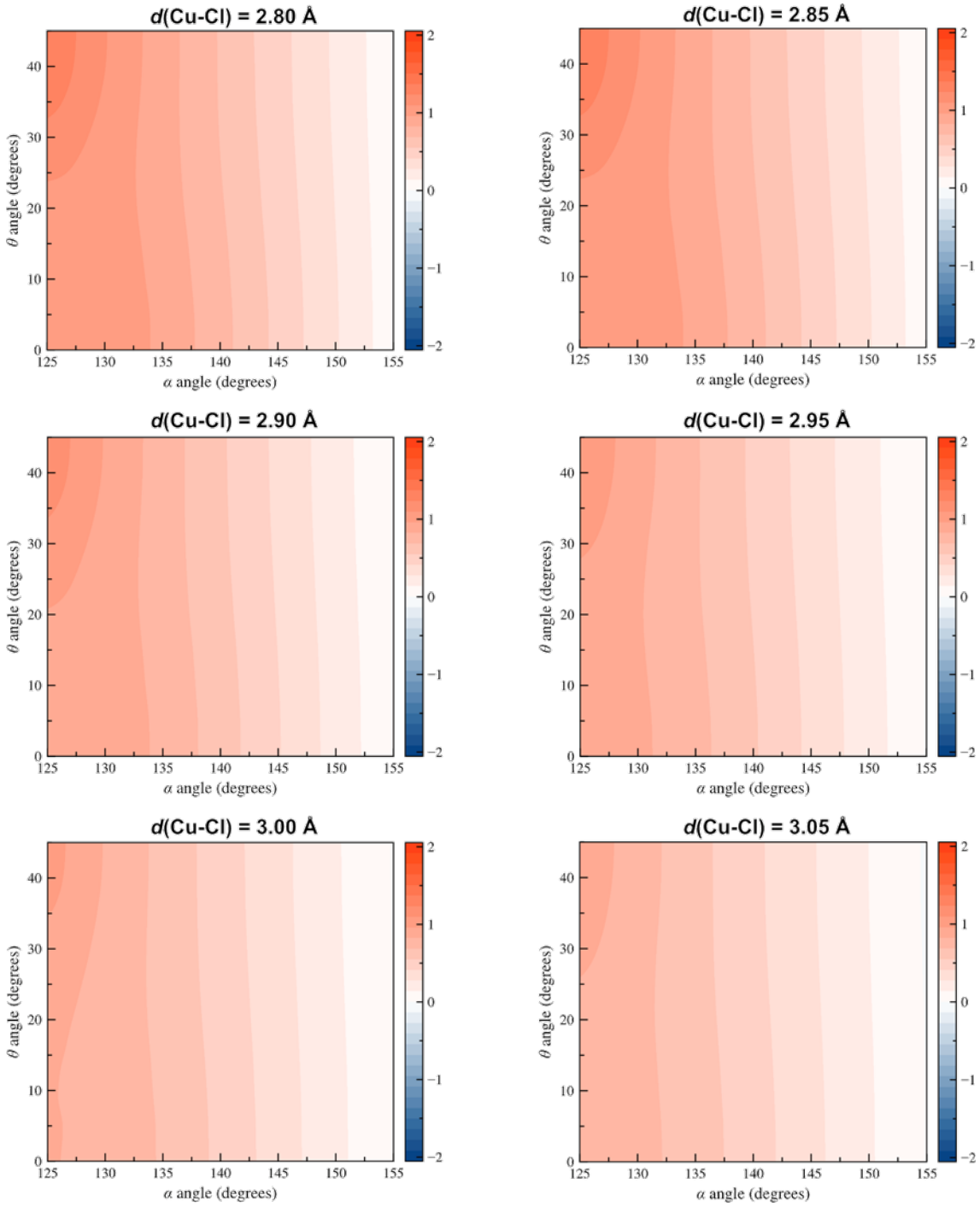

Figure S18. Contour maps of the dependence of the α and θ angles on the magnetic coupling constant in the molecular model of Fig. 4 for several Cu-Cl bond lengths in the range 2.80-3.05 Å at regular intervals of 0.05 Å.

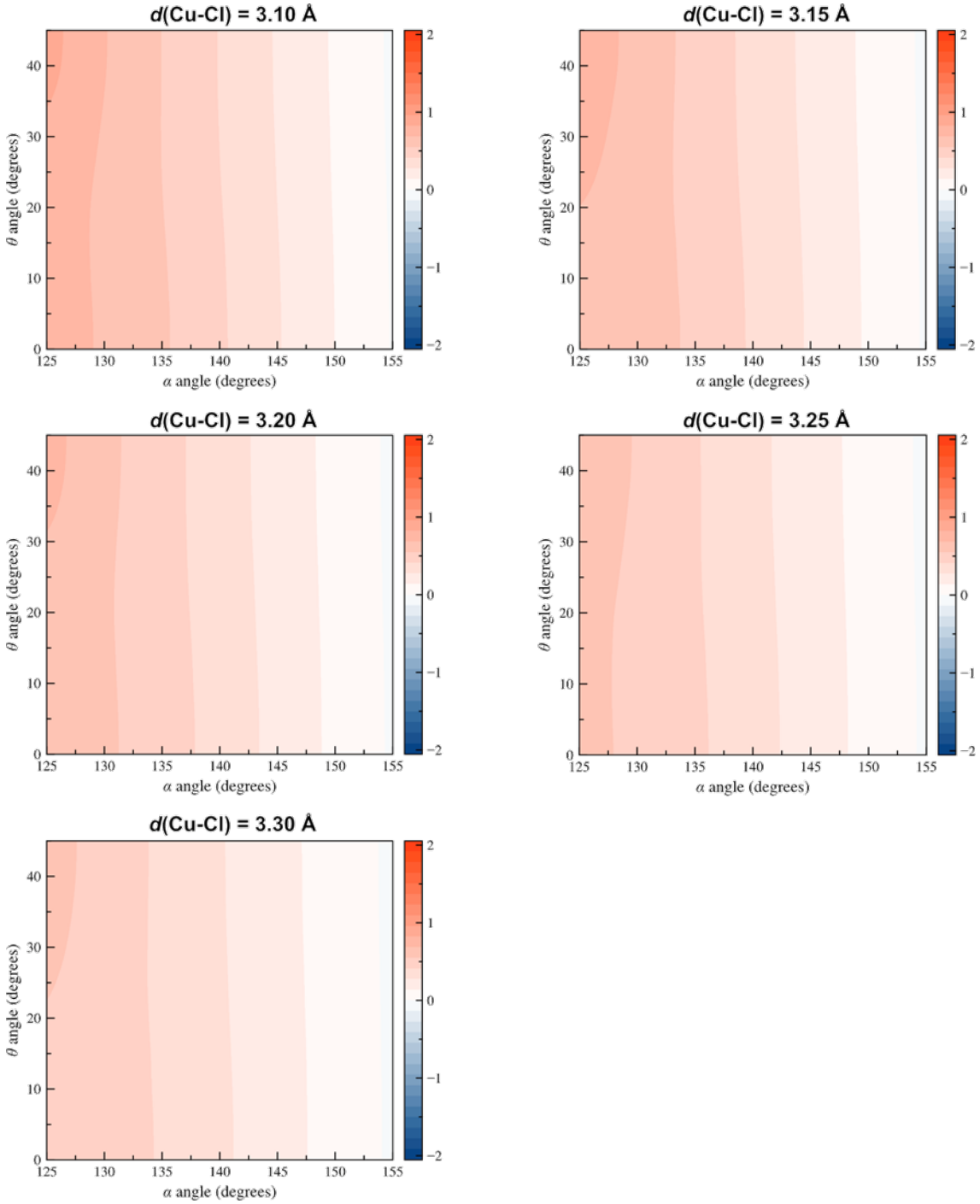

Figure S19. Contour maps of the dependence of the α and θ angles on the magnetic coupling constant in the molecular model of Fig. 4 for several Cu-Cl bond lengths in the range 3-10-3.25 Å at regular intervals of 0.05 Å.