Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Inducing Magnetic Communication in Caged Dinuclear Co(II) Systems

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Table S1. Crystallographic Data for **L1** and complex **6.**

Table S2. Selected Bond Distances (Å) and Angles for complexes **1-5.**

	L1		**8**	
Formula	$C_{37}H_{67}C_{15}N_8O_3$		$C_{44.5}H_{60}Cl_{10.5}Co_3N_{13.5}O_5S_{4.5}$	
FW, g.mol^{-1}	849.24		2405.78	
Crystal system	Triclinic		Monoclinic	
Space group	P-1		Pn	
a , Å	10.7107(2)		11.2372(6)	
b , Å	14.7465(3)		14.5050(8)	
c , Å	15.1857(3)		16.5974(9)	
α , °	108.500(1)		90	
β , °	93.433(1)		92.909(3)	
γ , °	94.351(1)		90	
V, Å^3	2259.05(8)		2701.8(3)	
Z	2		1	
ρ_{calcd}, g.cm^{-3}	1.248		1.479	
μ (Mo, Kα), mm^{-1}	0.364		1.165	
F(000)	908.0		1246	
measd/indep	32786 / 11133		30852/6606	
$R1(I > 2\ \sigma\ (I))$	0.0654		0.0562	
$wR2\ (I > 2\ \sigma\ (I))$	0.2065		0.1163	
GOF on F^2	1.046		1.051	

1 **2** **3** **4** **5**

$R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma w[(Fo)^2 - (Fc)^2]^2/\Sigma w[(Fo)^2]^2\}^{1/2}$

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Co(1)-O(1)	1.946(4)	1.985(4)			
Co(1)-N(1)	2.201(5)	2.106(4)	2.216(8)	2.236(3)	2.209(4)
Co(1)-N(2)	2.125(5)	2.123(5)	2.108(7)	2.116(4)	2.113(5)
Co(1)-N(3)	2.113(5)	2.111(5)	2.123(7)	2.111(4)	2.113(5)
Co(1)-N(4)	2.151(5)	2.215(4)	2.106(8)	2.109(4)	2.128(5)
Co(1)-N(5)			1.989(7)		
Co(1)-Cl(1)				2.364(5)	
Co(1)-Br(1)					2.4432(6)
Co(2)-O(2)	1.950(5)				
Co(2)-N(5)	2.198(5)	2.224(4)			
Co(2)-N(6)	2.127(5)	2.113(5)			
Co(2)-N(7)	2.118(5)	2.116(5)			
Co(2)-N(8)	2.201(8)	2.089(5)			
Co(2)-N(9)		1.998(4)			

Angles (°)

	1	**2**	**3**	**4**	**5**
O(1)-Co(1)-N(1)	177.75(17)	177.05(17)			
O(1)-Co(1)-N(2)	99.09(16)	101.18(17)			
O(1)-Co(1)-N(3)		99.95(18)			
O(1)-Co(1)-N(4)	95.9(2)	96.07(17)			
N(4)-Co(1)-N(1)	82.0(2)	81.21(17)	79.8(3)	80.65(17)	82.32(17)
N(3)-Co(1)-N(1)	81.4(2)	80.58(17)	81.1(3)	80.86(15)	81.70(18)
N(2)-Co(1)-N(1)	81.5(2)	81.19(16)	80.5(3)	80.69(19)	81.7(2)
N(3)-Co(1)-N(2)	108.60(18)	113.53(18)	112.3(3)	116.21(15)	118.10(18)
N(2)-Co(1)-N(4)	128.1(2)	118.7(2)	125.8(3)	117.48(16)	116.56(18)
N(3)-Co(1)-N(4)	117.0(2)	120.6(2)	113.7(3)	118.69(16)	119.48(19)
N(5)-Co(1)-N(3)			102.2(3)		
N(5)-Co(1)-N(4)			97.7(3)		
N(5)-Co(1)-N(2)			99.2(3)		
N(5)-Co(1)-N(1)			176.5(3)		
O(2)-Co(2)-N(5)	177.37(18)				
O(2)-Co(2)-N(6)	98.54(17)				
O(2)-Co(2)-N(7)	101.1(2)				
O(2)-Co(2)-N(8)	100.2(3)				
N(6)-Co(2)-N(5)	81.83(18)	80.95(17)			
N(7)-Co(2)-N(5)	81.2(2)	80.60(17)			
N(6)-Co(2)-N(8)	138.4(3)	118.3(2)			
N(9)-Co(2)-N(8)		96.13(18)			
N(9)-Co(2)-N(7)		101.05(18)			
N(8)-Co(2)-N(7)		120.2(2)			
N(9)-Co(2)-N(6)		99.91(17)			
N(8)-Co(2)-N(6)		118.3(2)			
N(7)-Co(2)-N(6)		114.3(2)			
N(9)-Co(2)-N(5)		177.55(18)			

N(8)-Co(2)-N(5)	81.45(18)		
N(4)-Co(1)-Cl(1)/Br(1)		99.04(12)	98.66(12)
N(3)-Co(1)-Cl(1)/Br(1)		100.01(12)	97.62(12)
N(2)-Co(1)-Cl(1)/Br(1)		98.74(12)	98.04(13)
N(1)-Co(1)-Cl(1)/Br(1)		179.11(14)	179.01(11)
Co(1)-Cl(1)-Co(1´)		179.66(12)	
Co(1)-Br(1)-Co(1´)			179.06(5)

Table S3. Force Constants *k* in Dines cm^{-1} for **L1** and complexes **1-5.**

	$\kappa_{O\text{-}H\ st}$ x 10^5	$\kappa_{N\text{-}H\ st}$ x 10^5	$\kappa_{C\text{-}H\ st}$ x 10^5	$\kappa_{C=O\ st}$	$\kappa_{C=N\ st}$ x 10^6	$\kappa_{N=N\ st}$ x 10^6	$\kappa_{C=C\ st}$ x 10^5	$\kappa_{Cl\text{-}O\ st}$ x 10^5	$\kappa_{C\text{-}H\ \delta}$ x 10^4	$\kappa_{C\text{-}H\ \delta\ ar}$ x 10^4
L1		5.9	4.3				7.4		3.0/2.6/2.3	1.9
1		5.8	4.5	$9.9x10^5$			7.4	7.4	3.4/3.1/2.7	2.1
2		5.8	4.5		2.0		7.5	7.2	3.4/3.1/2.6	2.1
3		5.7	4.5			2.0/1.7	7.3	7.3	3.4/3.1/2.7	2.2
4/5		5.9	4.7				7.7	7.2	3.6/3.2/2.7	2.1

Table S4. Wavelengths (λ) and molar absorptivities (ε) for the electronic transitions in **1-5.**

	λ (nm) ε ($Lmol^{-1}cm^{-1}$)	λ (nm) ε ($Lmol^{-1}cm^{-1}$)	λ (nm) ε ($Lmol^{-1}cm^{-1}$)	λ (nm) ε ($Lmol^{-1}cm^{-1}$)	λ (nm) ε ($Lmol^{-1}cm^{-1}$)
1	460.0 259.4	476.5 267.47	602 256.4	-	705.0 95.6
2	466 231.9	466.0 224.4	601.5 234.8	656 173.5	658 82.3
3	460.0 187.42	486.0 181.4	599.6 290.2	-	708.0 80.6
4	-	509.0 112.1	609.0 161.7	683.0 54.1	796.0 26.7
5	-	479.5 132.6	606.0 173.4	685.0 126.5	844.0 16.0

Table S5. Overlap integrals calculations for complexes **1**-**5**.

Co2-OAc	α/β	$d_{x^2-y^2}$	d_{xy}	d_{z^2}
	$d_{x^2-y^2}$	0.023	0.006	0.080
	d_{xy}	0.007	0.015	0.005
	d_{z^2}	0.004	0.013	0.074

Co2-OCN	α/β	$d_{x^2-y^2}$	d_{xy}	d_{z^2}
	$d_{x^2-y^2}$	0.001	0.001	0.001
	d_{xy}	0.002	0.001	0.003
	d_{z^2}	0.000	0.018	0.029

Co2-N3	α/β	$d_{x^2-y^2}$	d_{xy}	d_{z^2}
	$d_{x^2-y^2}$	0.004	0.005	0.004
	d_{xy}	0.001	0.023	0.001
	d_{z^2}	0.011	0.004	0.027

Co2-Cl	α/β	$d_{x^2-y^2}$	d_{xy}	d_{z^2}
	$d_{x^2-y^2}$	0.003	0.064	0.034
	d_{xy}	0.064	0.017	0.078
	d_{z^2}	0.034	0.078	0.157

Co2-Br	α/β	$d_{x^2-y^2}$	d_{xy}	d_{z^2}
	$d_{x^2-y^2}$	0.036	0	0.001
	d_{xy}	0	0.034	0.014
	d_{z^2}	0.001	0.001	0.299

Table S6. Contribution to *D* from different spin states for complexes **1**, **2** and **3**.

D = -16.370916 cm-1
E/D = 0.218828

Individual contributions to D-tensor:

Block	Mult	Root	D	E
0	4	0	0.000	0.000
0	4	1	-35.816	0.076
0	4	2	3.290	-2.953
0	4	3	7.218	-7.169
0	4	4	7.189	7.363
0	4	5	0.595	-0.621
0	4	6	0.369	0.372
0	4	7	0.000	-0.000
0	4	8	0.069	0.071
0	4	9	0.059	-0.063
1	2	0	-0.977	-1.277
1	2	1	-0.475	0.580
1	2	2	0.554	-0.011
1	2	3	-0.085	0.048
1	2	4	0.027	-0.003
1	2	5	2.289	-0.166
1	2	6	1.420	-0.012
1	2	7	-1.634	0.897
1	2	8	1.563	-0.373
1	2	9	-0.297	-0.300
1	2	10	-0.132	0.139
1	2	11	-0.014	0.012
1	2	12	0.282	-0.000
1	2	13	-0.042	0.021
1	2	14	-0.152	0.160
1	2	15	-0.001	-0.022
1	2	16	-0.335	0.287
1	2	17	-0.182	-0.014
1	2	18	-0.416	-0.557
1	2	19	-0.048	0.121
1	2	20	-0.266	0.011
1	2	21	-0.496	-0.364
1	2	22	-0.084	0.084
1	2	23	0.504	0.010
1	2	24	-0.129	0.149
1	2	25	-0.088	-0.100
1	2	26	0.002	-0.000
1	2	27	0.000	0.001
1	2	28	-0.002	0.002
1	2	29	-0.184	0.164
1	2	30	-0.138	-0.141
1	2	31	0.172	-0.000
1	2	32	-0.007	0.005
1	2	33	-0.002	0.002
1	2	34	0.001	-0.001
1	2	35	0.054	-0.001
1	2	36	0.000	0.000
1	2	37	-0.002	-0.003
1	2	38	-0.013	0.014
1	2	39	-0.013	-0.020

D = 3.598602 cm-1
E/D = 0.309882

Individual contributions to D-tensor:

Block	Mult	Root	D	E
0	4	0	0.000	-0.000
0	4	1	12.125	9.689
0	4	2	-1.140	-0.001
0	4	3	10.274	-7.870
0	4	4	-17.147	0.003
0	4	5	0.400	-0.253
0	4	6	-0.647	0.001
0	4	7	-0.000	-0.000
0	4	8	-0.128	-0.000
0	4	9	0.061	-0.035
1	2	0	1.619	-0.000
1	2	1	-0.571	0.157
1	2	2	-0.134	-0.056
1	2	3	0.002	-0.000
1	2	4	0.000	0.000
1	2	5	-0.103	-0.102
1	2	6	-3.053	-3.045
1	2	7	3.511	0.007
1	2	8	-2.751	1.879
1	2	9	0.223	0.000
1	2	10	-0.082	0.033
1	2	11	0.010	-0.000
1	2	12	-0.090	-0.076
1	2	13	0.016	-0.000
1	2	14	-0.264	0.143
1	2	15	0.429	-0.001
1	2	16	0.311	-0.000
1	2	17	-0.229	0.129
1	2	18	0.694	-0.001
1	2	19	-0.194	0.025
1	2	20	-0.014	0.016
1	2	21	-0.058	0.069
1	2	22	0.412	0.002
1	2	23	-0.411	-0.106
1	2	24	-0.315	0.141
1	2	25	0.577	-0.004
1	2	26	0.021	0.001
1	2	27	-0.014	0.011
1	2	28	0.085	0.000
1	2	29	0.033	0.052
1	2	30	0.051	0.040
1	2	31	-0.094	-0.035
1	2	32	0.005	0.000
1	2	33	-0.001	0.001
1	2	34	0.000	-0.000
1	2	35	-0.040	-0.017
1	2	36	-0.001	0.000
1	2	37	0.003	0.000
1	2	38	0.039	0.000
1	2	39	-0.017	0.001

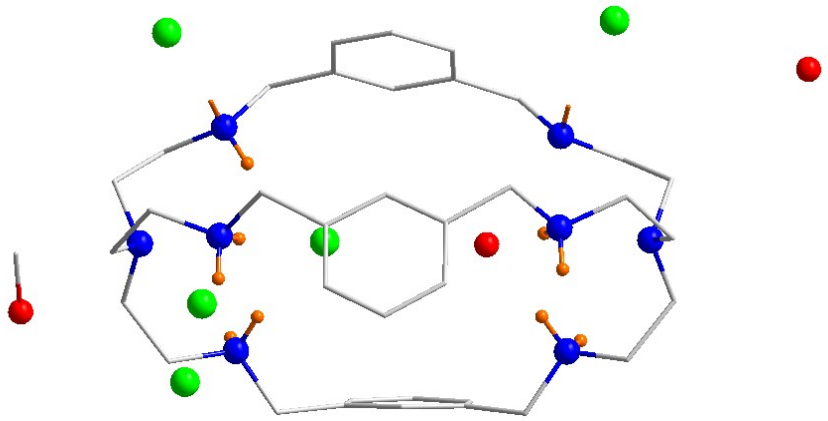


Figure S1. X-ray structure of the azacryptand ligand. Only the H atoms of the ammonium groups are shown for clarity. Colour code: Blue (N), red (O), grey (C), orange (H), Green (Cl).

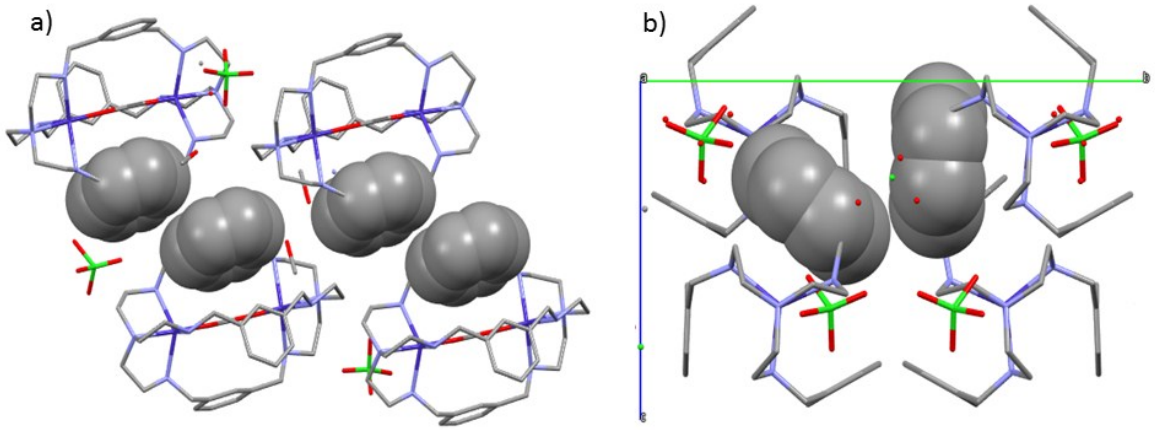


Figure S2. π–π interactions for a) **2** and b) **4**. Colour code: Purple (Co), blue (N), red (O), grey (C), bright green (Cl).

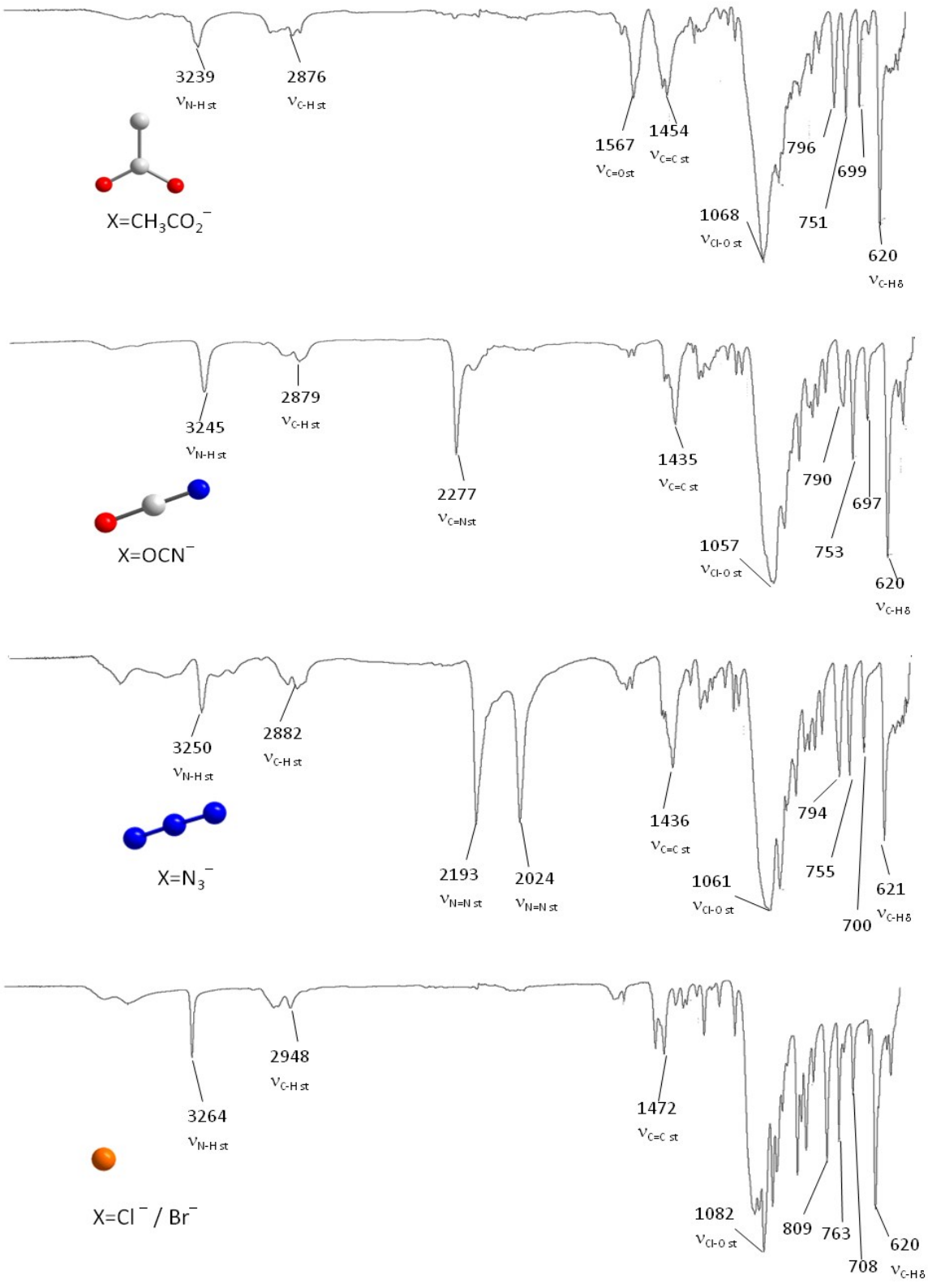


Figure S3. IR spectra of complexes **1-5** highlighting the main peaks in the 4000-400 cm^{-1} zone.

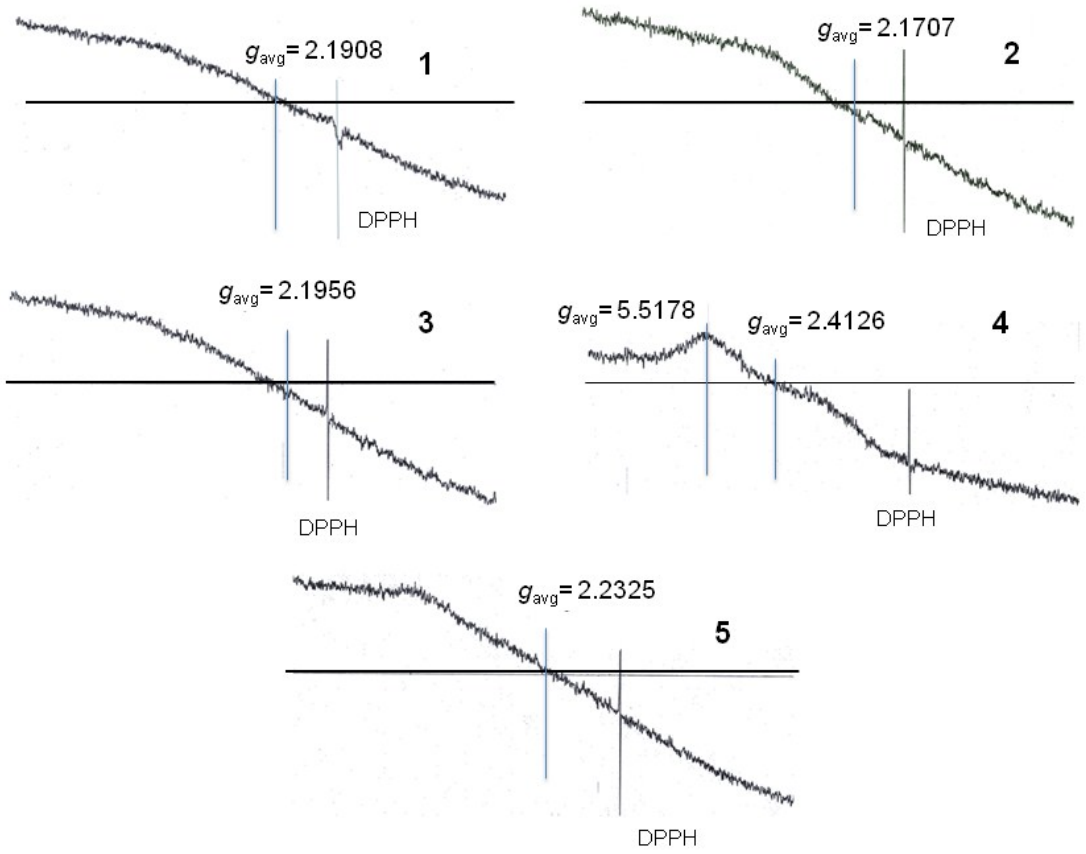


Figure S4. EPR spectra in CH_3CN at 77 K of complexes **1-5** showing broad signals with g_{avg} values. Slow sweep (min): 2; swp (mT): 7.9 x 100; Mod. Wid. (mT): 0.2 x 1; Amplitd: 5 x 1000; Time Cnst. (ms): 0.03; Power (mW): 1.

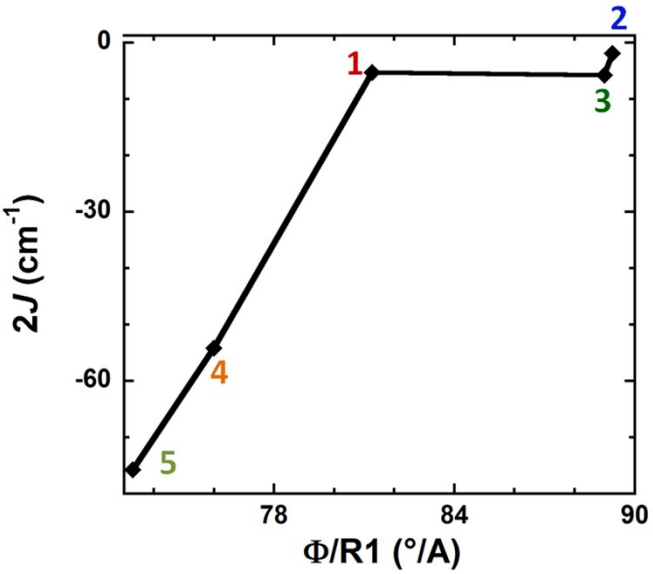


Figure S5. Plot of 2*J vs* Φ/R1 for compounds **1-5**.

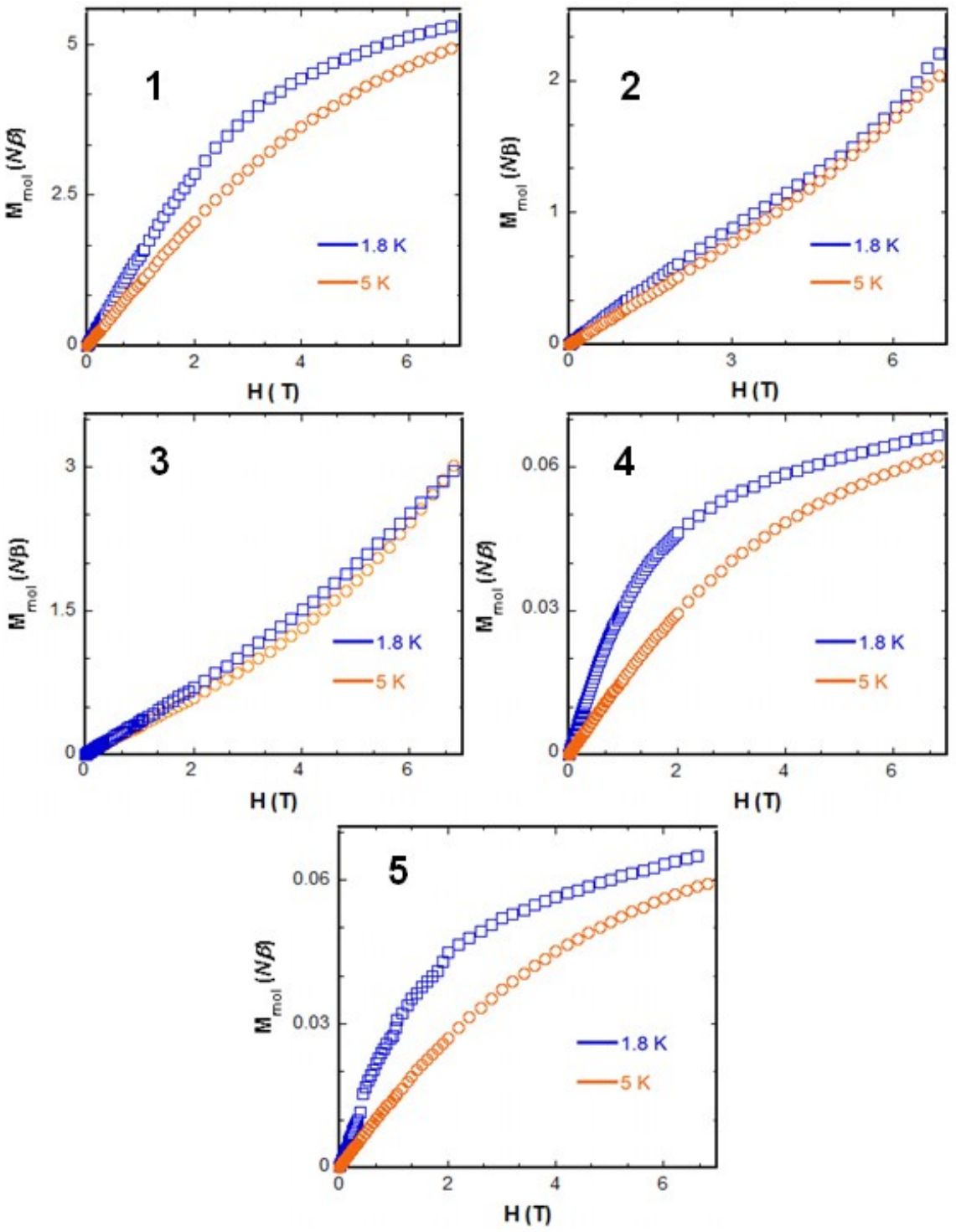


Figure S6. Plots of M_{mol} *vs.* H at 1.8 K (blue line) and 5 K (orange line) for compounds **1-5**.

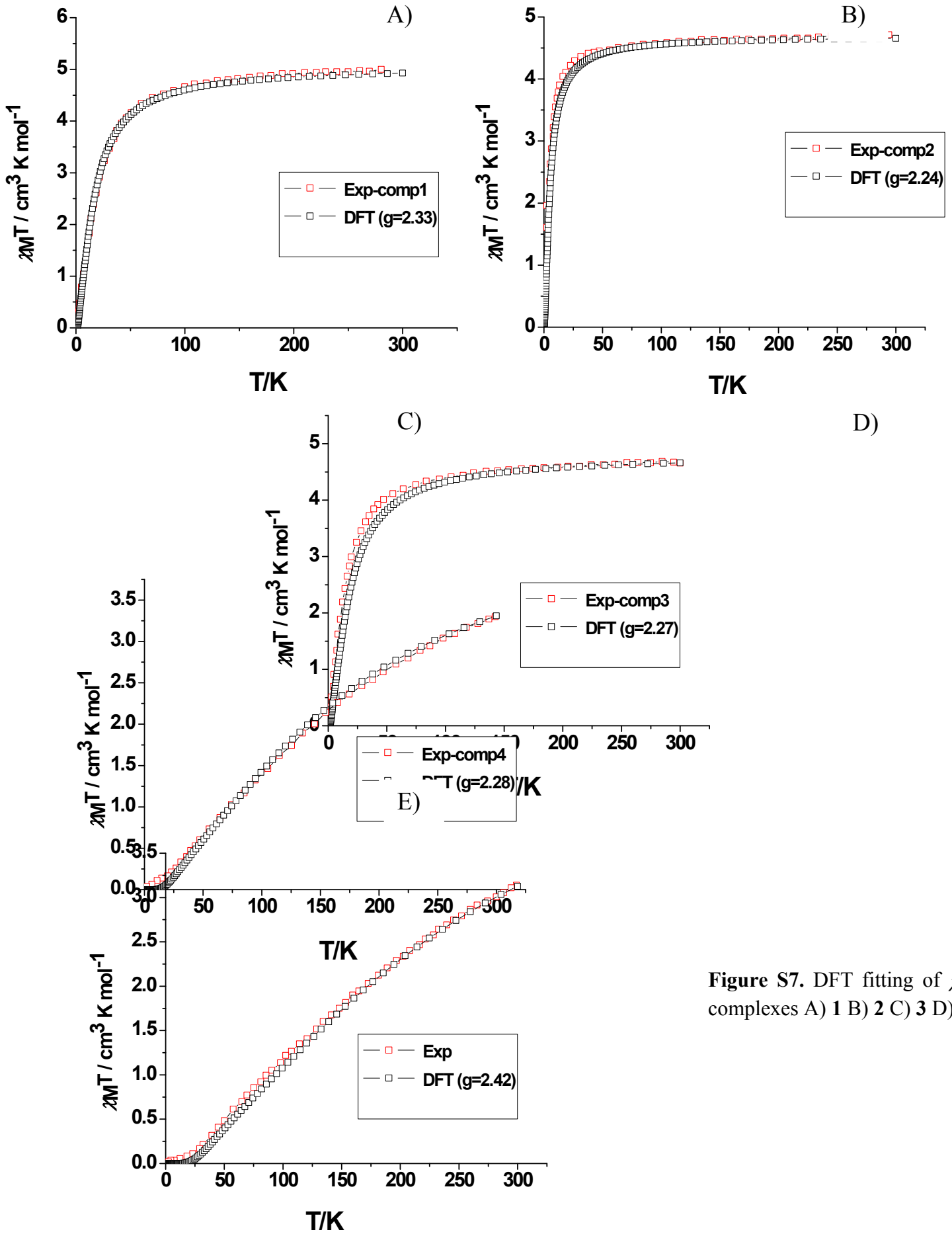


Figure S7. DFT fitting of χT *vs.* complexes A) **1** B) **2** C) **3** D) **4** and

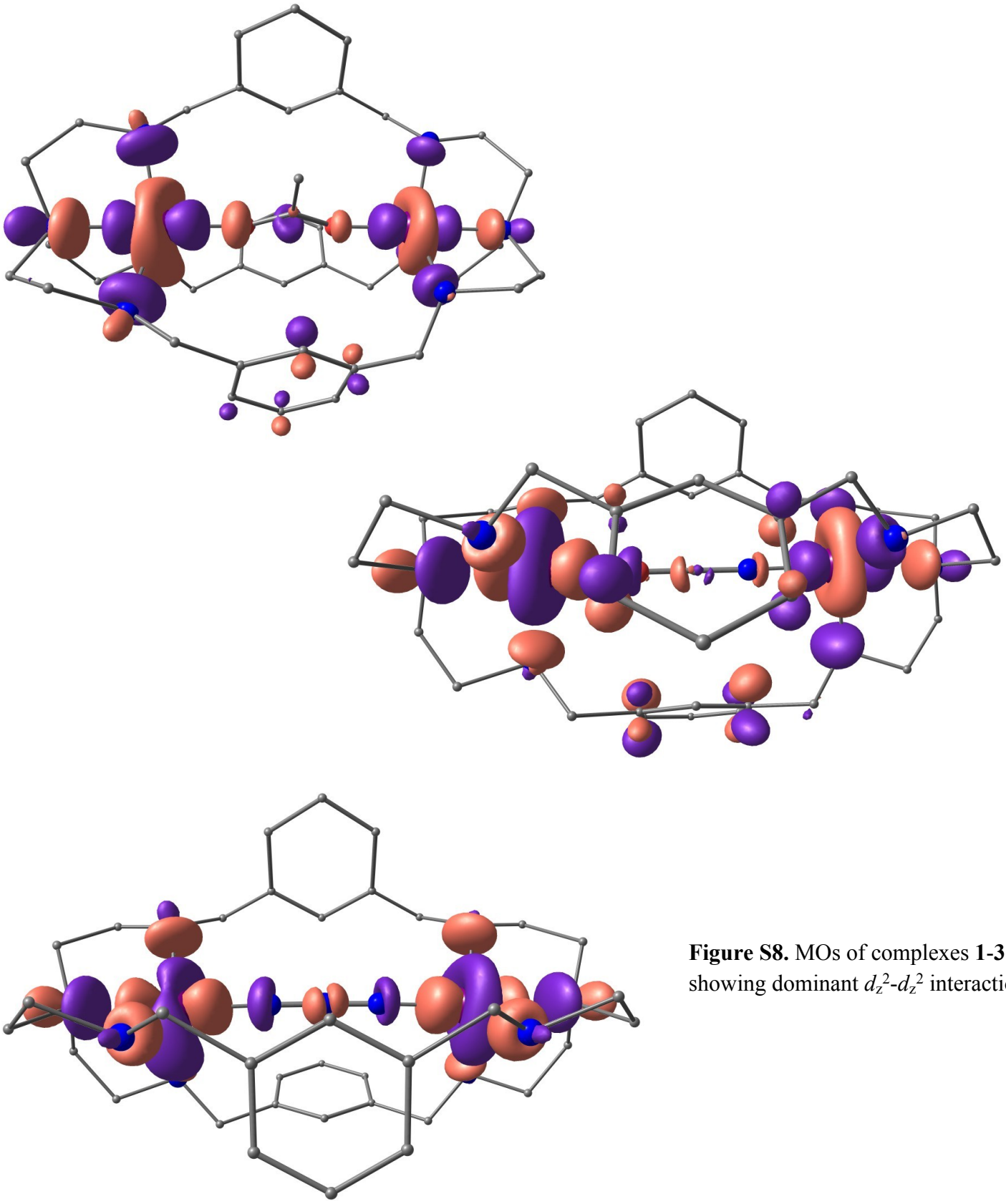


Figure S8. MOs of complexes **1-3** showing dominant d_z^2-d_z^2 interaction.

A) B)

0.03 0.03

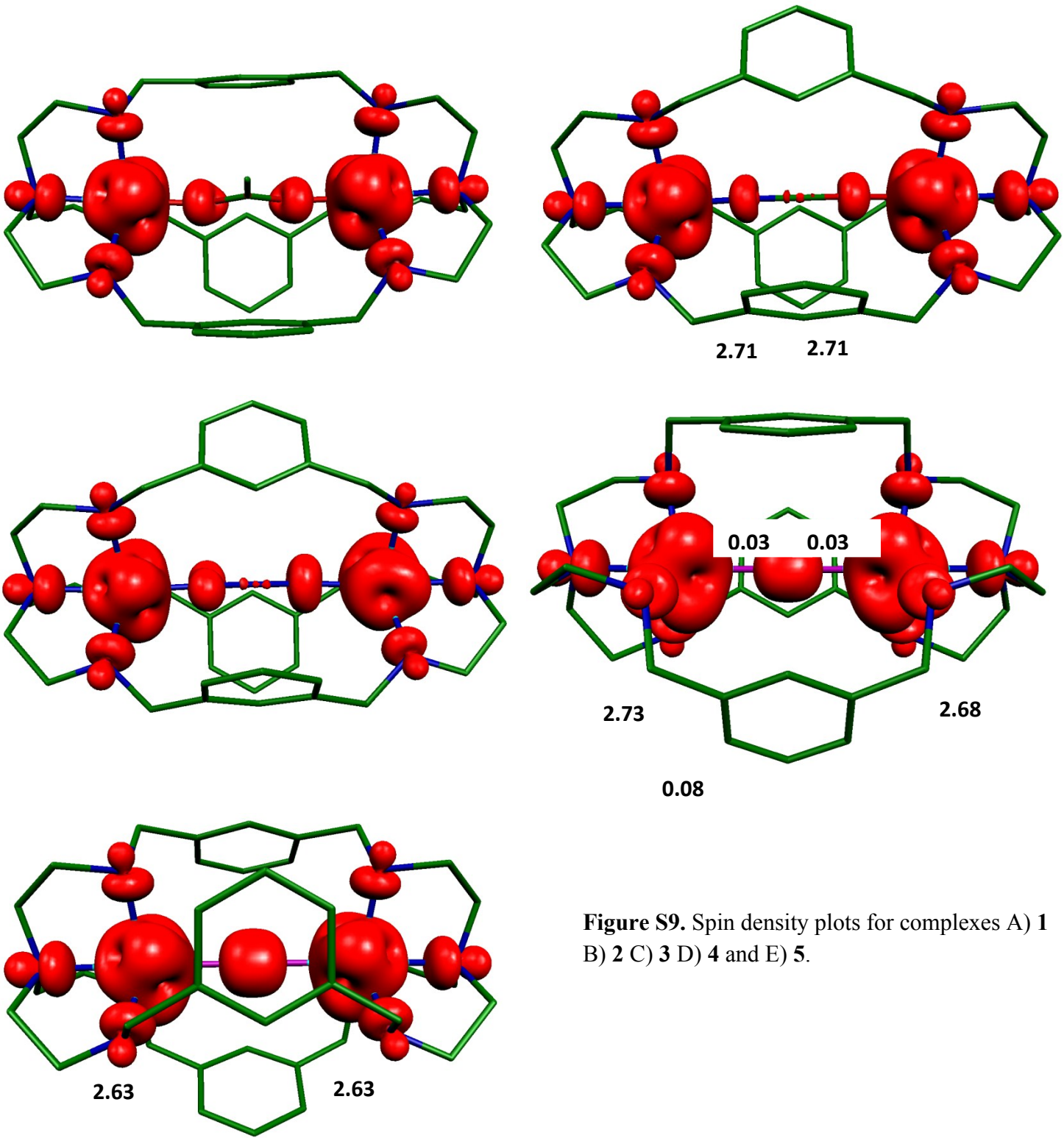
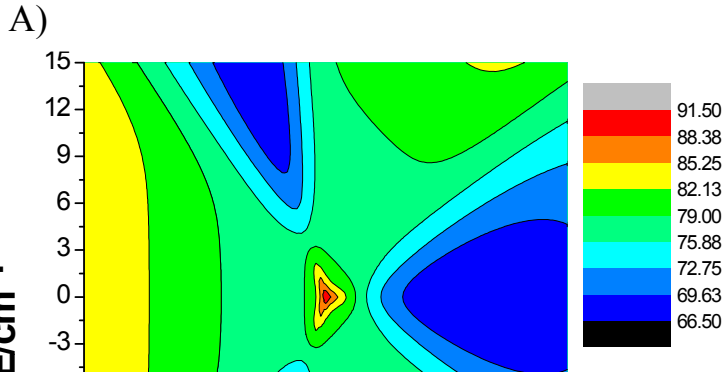
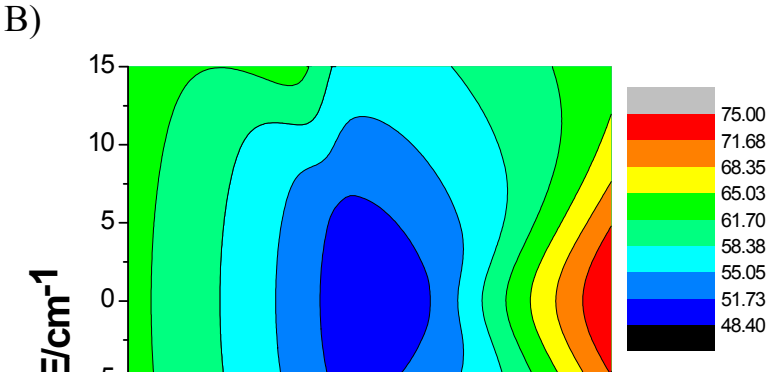


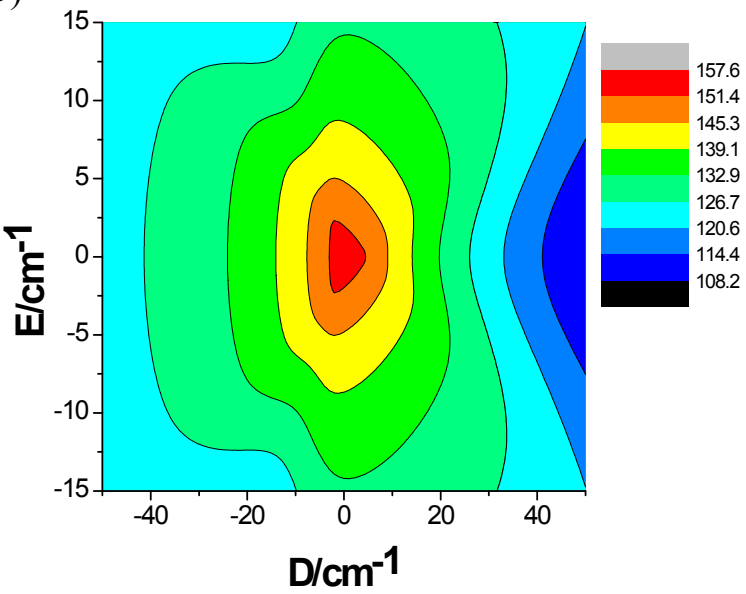
Figure S9. Spin density plots for complexes A) **1** B) **2** C) **3** D) **4** and E) **5**.





C)

D)



E)

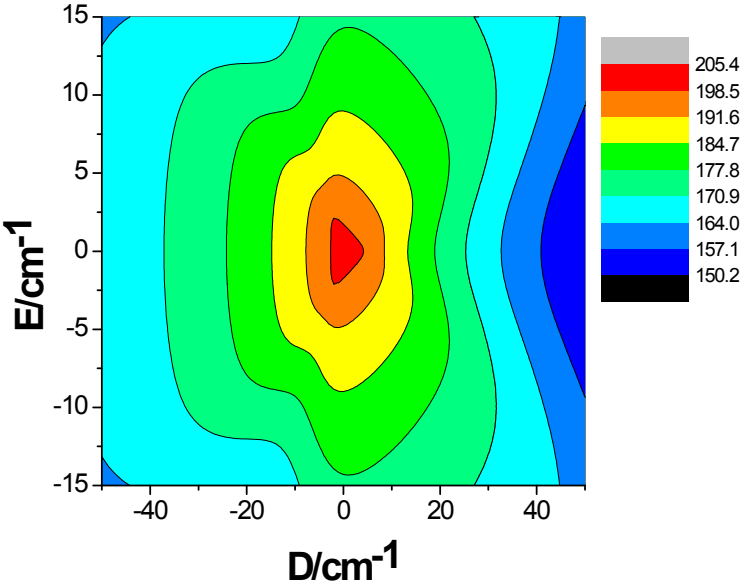


Figure S10. The magnetic data can be fitted using multiple parameters using PHI software which is represented in the 2-dimentional plot for models A) **1** B) **2** c) **3** d) **4** and e) **5**. This clearly shows a range of parameters can yield a good fit to the magnetic data.