Supplementary Information

Magneto-structural correlations in a family of di-alkoxo bridged chromium dimers

Hector W. L. Fraser,[a] Gary S. Nichol,[a] Gunasekaran Velmurugan,[b] Gopalan Rajaraman[b*] and Euan K. Brechin[a*]

[a.]EaStCHEM School of Chemistry, The University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ Scotland, UK.
E-mail: E.Brechin@ed.ac.uk
Tel: +44 (0)131-650-7545
[b.]Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, 400076, India.
E-Mail: rajaraman@chem.iitb.ac.in

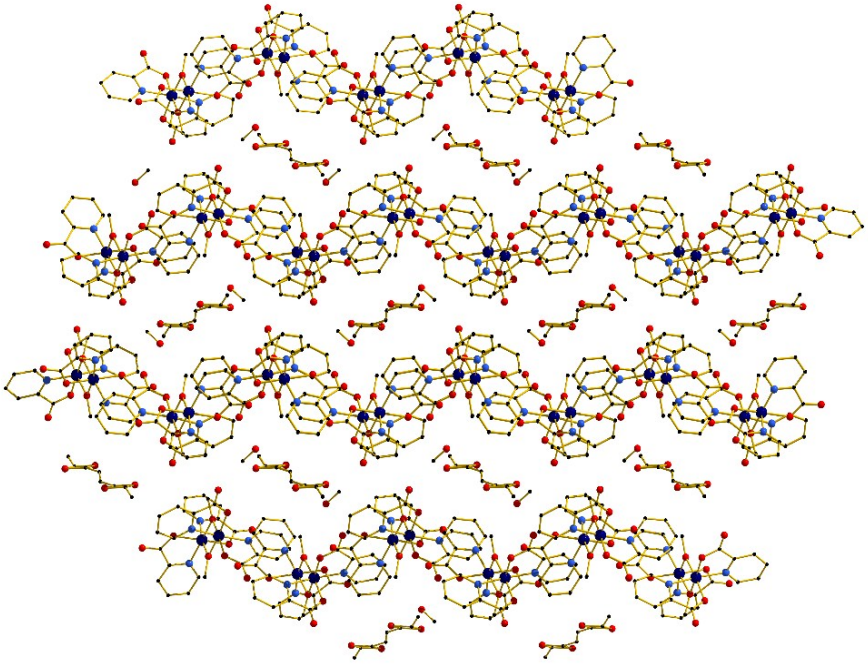

Figure S1. Packing diagram for compound **1** viewed along the *a*-axis.

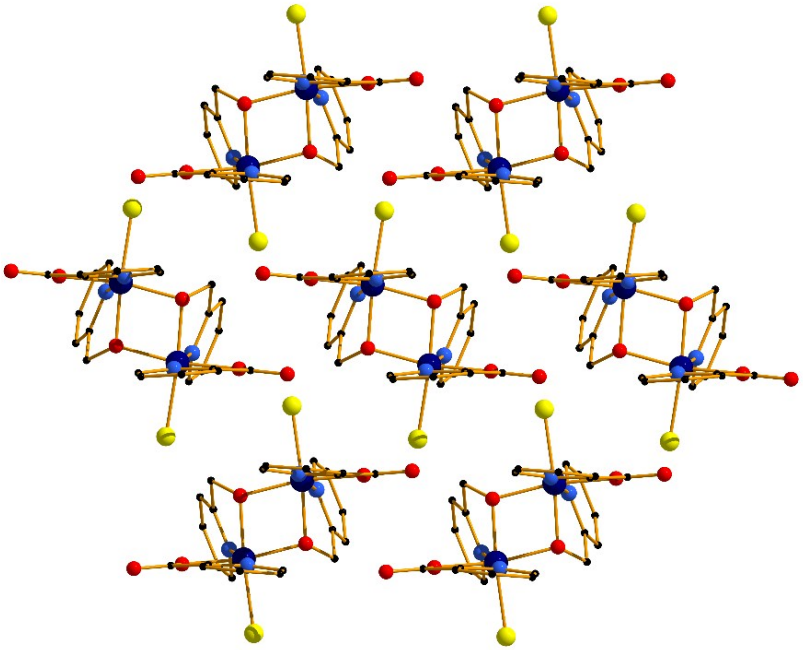

Figure S2. Packing diagram for compound **2** viewed along the *c*-axis. Compound **3** displays a similar extended structure.

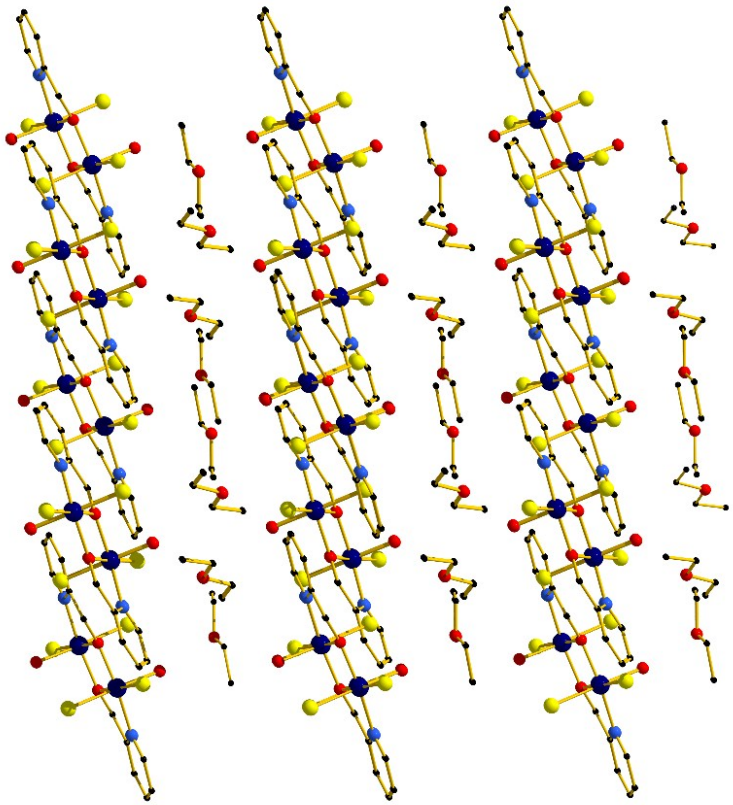

Figure S3. Packing diagram for compound **4** viewed along the *c*-axis.

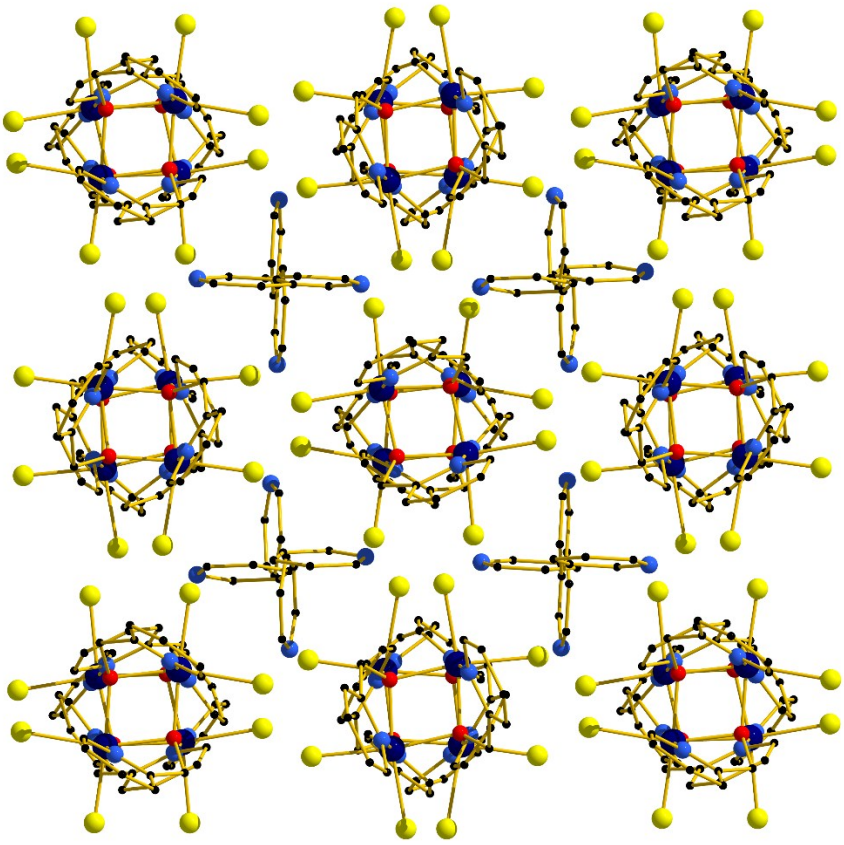

Figure S4. Packing diagram for compound **5** viewed along the *c*-axis.

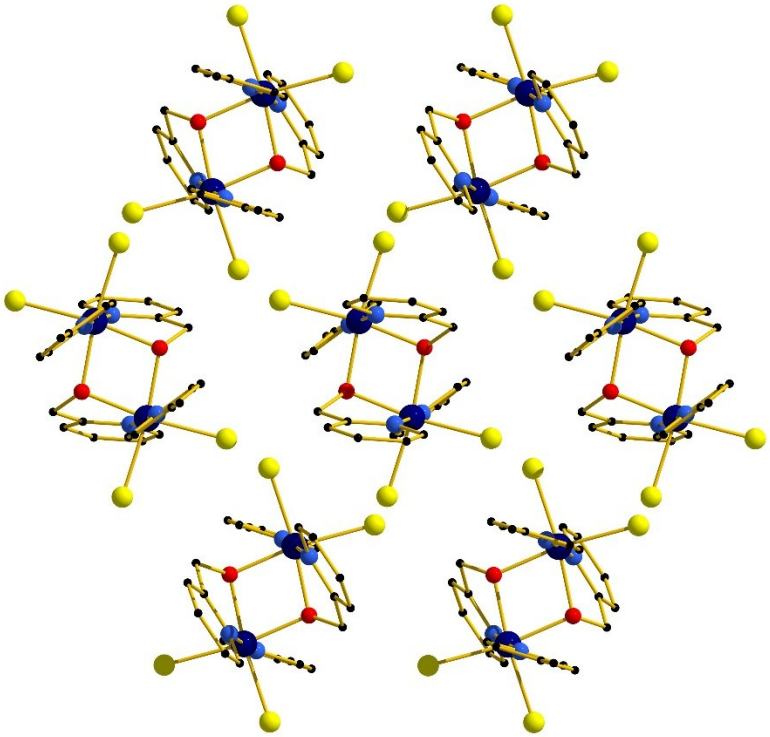

Figure S5. Packing diagram for compound **6** viewed along the *b*-axis.

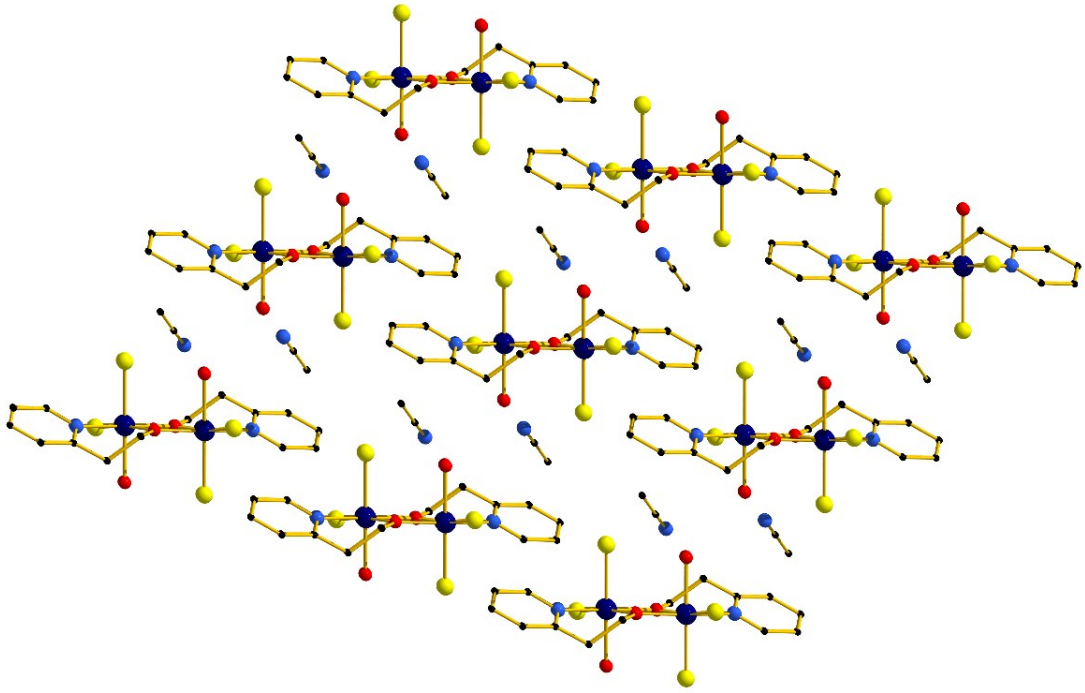

Figure S6. Packing diagram for compound **7** viewed along the *b*-axis.

Table S1. Crystallographic information for compounds **1**-**6**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{28.5}H_{29}Cr_2N_4O_{11}$	$C_{24}H_{20}Cl_2Cr_2N_4O_6$	$C_{24}H_{20}Br_2Cr_2N_4O_6$	$C_{20}H_{36}Cl_4Cr_2N_2O_6$	$C_{32}H_{32}Cl_4Cr_2N_6O_2$	$C_{24}H_{26}Cl_4Cr_2N_4O_2$
$D_{calc.}$/ g cm^{-3}	1.419	1.693	1.879	1.520	1.531	1.625
μ/mm^{-1}	0.717	1.136	4.019	1.183	8.539	10.720
Formula Weight	707.56	635.34	724.26	646.31	778.43	648.29
Colour	pink	brown	light purple	green	dark green	blue
Shape	block	block	prism	block	block	block
Size/mm^3	0.25x0.12x0.09	0.33x0.18x0.18	0.24x0.10x0.09	0.19x0.16x0.11	0.24x0.14x0.05	0.20×0.09×0.03
T/K	120.00	120.00	120.0	120.0	120.0	120.0
Crystal System	monoclinic	orthorhombic	orthorhombic	triclinic	tetragonal	monoclinic
Flack/Hooft Parameters	-	-0.003(5)/-0.018(4)	0.010(7)/0.028(7)	-	(n/a)/0.255(8)	-
Space Group	$P2_1/n$	$Pnn2$	$Pnn2$	P-1	$I4_1$	P2/c
a/Å	12.2931(8)	7.81306(10)	7.8068(2)	9.7732(4)	16.2418(2)	14.29325(19)
b/Å	21.3092(16)	12.17220(15)	12.2423(4)	10.4693(3)	16.2418(2)	14.06348(14)
c/Å	13.2192(8)	13.10384(16)	13.3916(4)	14.0067(7)	25.6069(6)	14.8511(2)
α/°	90	90	90	92.473(4)	90	90
β/°	106.939(7)	90	90	99.099(4)	90	117.3958(17)
γ/°	90	90	90	91.960(3)	90	90
V/Å^3	3312.6(4)	1246.20(3)	1279.88(7)	1412.58(10)	6755.0(2)	2650.46(7)
Z (Z')	4 (1)	2 (0.5)	2 (0.5)	2 (1)	8 (1)	4 (1)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	1.54178	1.54178
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	CuK_α	CuK_α
Θ_{min}/° - Θ_{max}/°	3.222 - 24.996	3.035 - 32.892	3.042 - 29.769	3.288 - 28.854	4.938 - 76.392	3.142 – 76.778
Measured Refl.	47599	45650	11349	22598	28737	43244
Independent Refl.	5824	4514	3209	6514	6396	5513
Reflections Used	4892	4406	3011	5624	5590	5054
R_{int}	0.0970	0.0356	0.0369	0.0452	0.0730	0.0554
Parameters	454	212	172	324	432	327
Restraints	31	1	1	6	247	0
Largest Peak	0.768	0.308	0.423	0.829	0.830	0.524
Deepest Hole	-0.585	-0.300	-0.500	-0.632	-0.608	-0.677
GooF	1.151	1.051	1.066	1.266	1.044	1.038
wR_2 (all data) (wR_2)	0.2129 (0.2054)	0.0528 (0.0522)	0.0570 (0.0549)	0.1652 (0.1608)	0.2107 (0.1952)	0.1227 (0.1198)
R_1 (all data) (R_1)	0.0979 (0.0830)	0.0225 (0.0215)	0.0344 (0.0304)	0.0862 (0.0728)	0.0858 (0.0739)	0.0455 (0.0428)

Table S2. Crystallographic information for compounds **7**-**8**.

Compound	**7**	**8**
Formula	$C_{18}H_{26}Cl_4Cr_2N_4O_4$	$C_{14}H_{16}Cl_2CrN_3O_2$
$D_{calc.}$/ g cm^{-3}	1.628	1.713
μ/mm^{-1}	11.459	1.145
Formula Weight	608.23	381.20
Colour	brown	green
Shape	block	block
Size/mm^3	0.09x0.06x0.04	0.22x0.05x0.04
T/K	120.0	120.0
Crystal System	triclinic	tetragonal
Flack/Hooft Parameters	-	-
Space Group	P-1	$P4_2/nbc$
a/Å	8.2906(3)	15.4761(3)
b/Å	8.5467(3)	15.4761(3)
c/Å	10.1679(4)	12.3453(3)
α/°	112.400(4)	90
β/°	101.243(3)	90
γ/°	102.099(3)	90
V/Å^3	620.49(4)	2956.82(13)
Z (Z')	1 (0.5)	8 (0.5)
Wavelength/Å	1.54178	0.71073
Radiation type	CuK_α	MoK_α
Θ_{min}/° - Θ_{max}/°	4.938 - 76.392	3.107 - 26.369
Measured Refl.	10079	134457
Independent Refl.	2577	1520
Reflections Used	2421	1516
R_{int}	0.0566	0.0725
Parameters	153	90
Restraints	3	3
Largest Peak	0.788	0.452
Deepest Hole	-0.520	-0.358
GooF	1.062	1.330
wR_2 (all data) (wR_2)	0.1287 (0.1262)	0.1087 (0.1086)
R_1 (all data) (R_1)	0.0488 (0.0466)	0.0491 (0.0489)

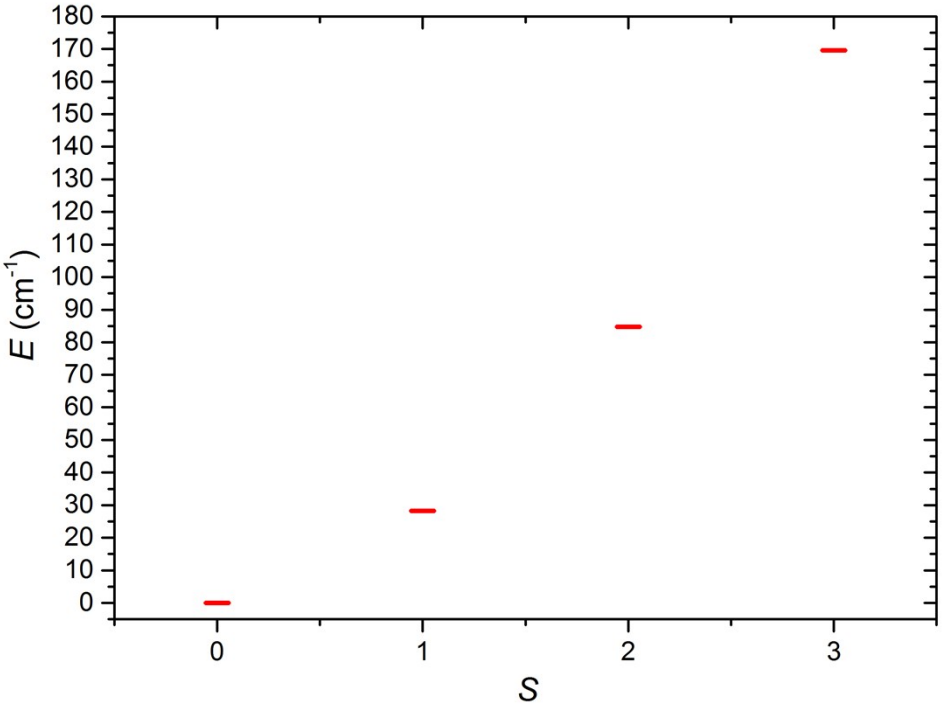

Figure S7. Energy levels of compound **1** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

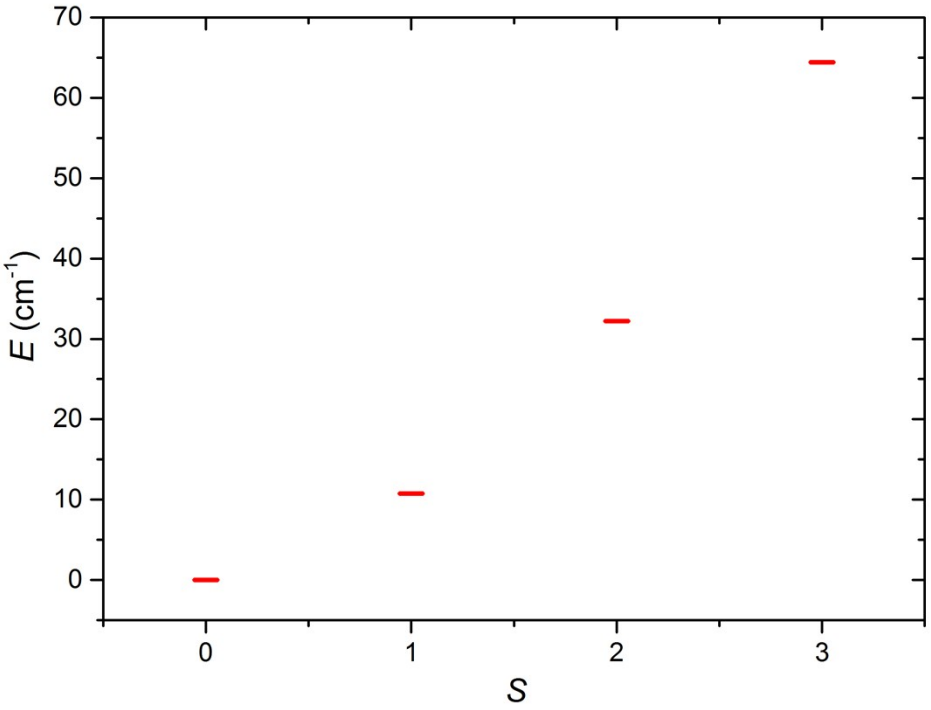

Figure S8. Energy levels of compound **2** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

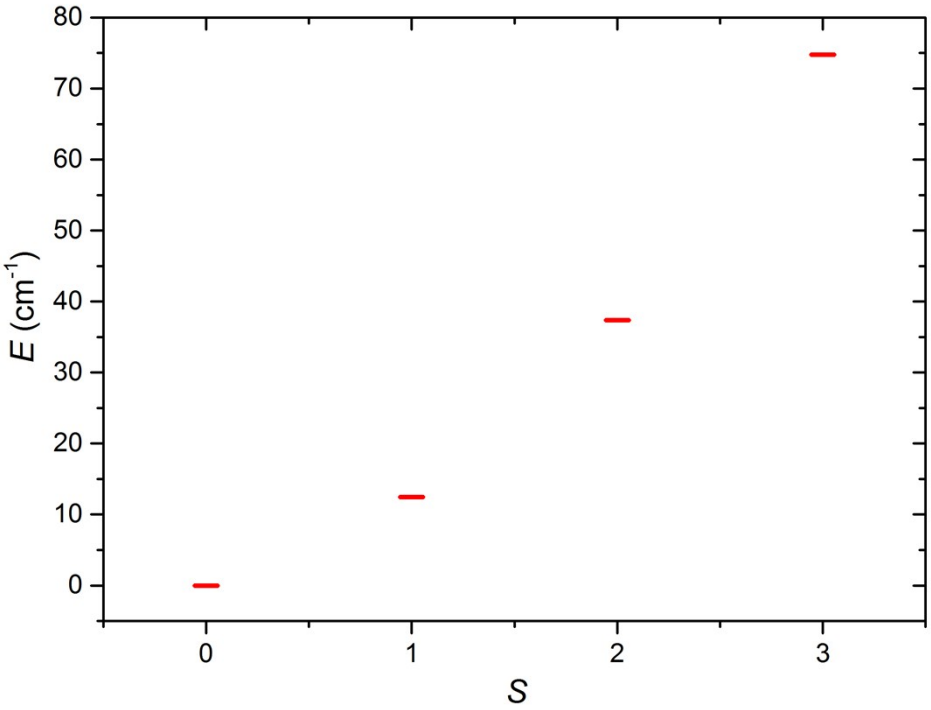

Figure S9. Energy levels of compound **3** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

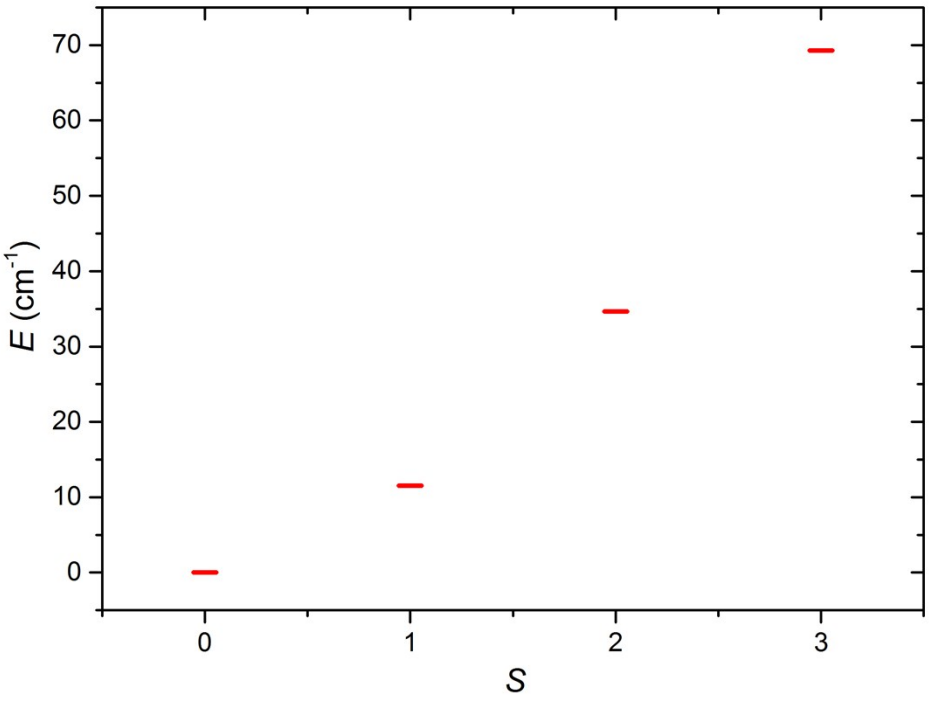

Figure S10. Energy levels of compound **4** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

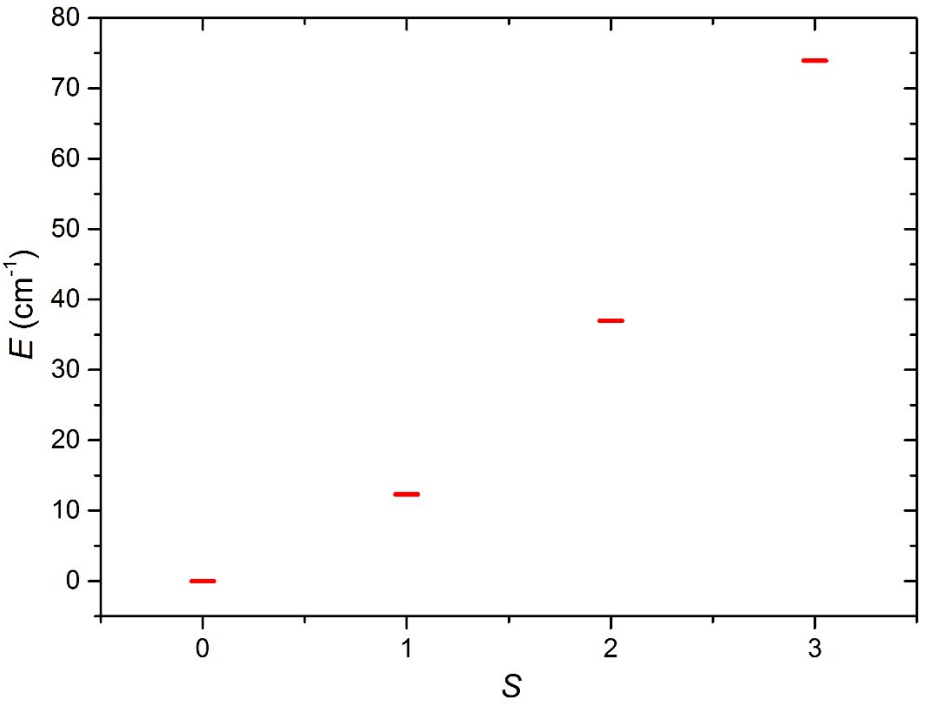

Figure S11. Energy levels of compound **5** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

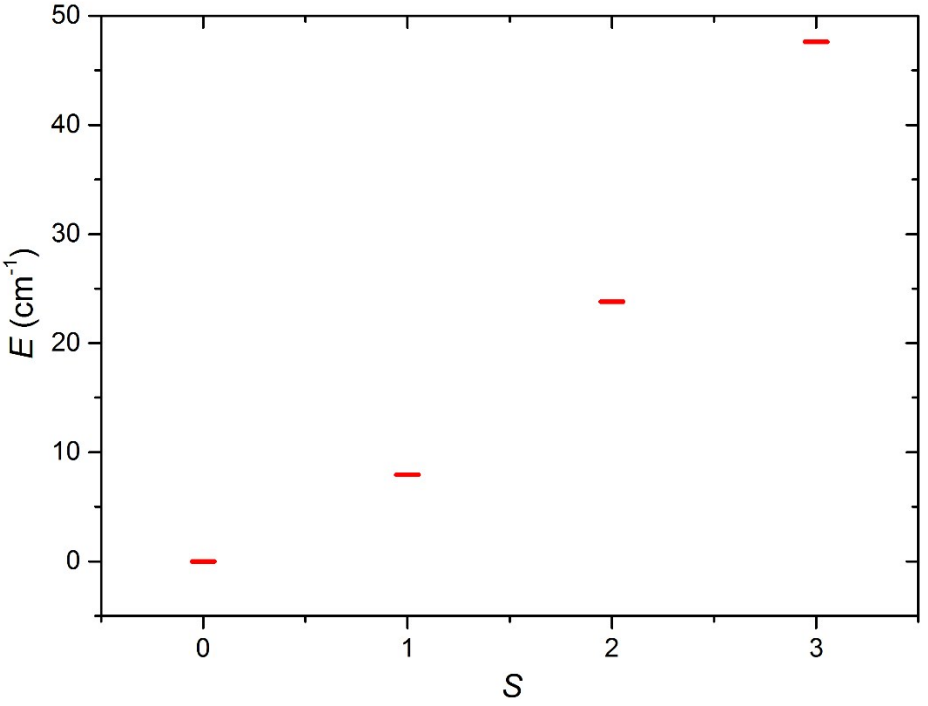

Figure S12. Energy levels of compound **6** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

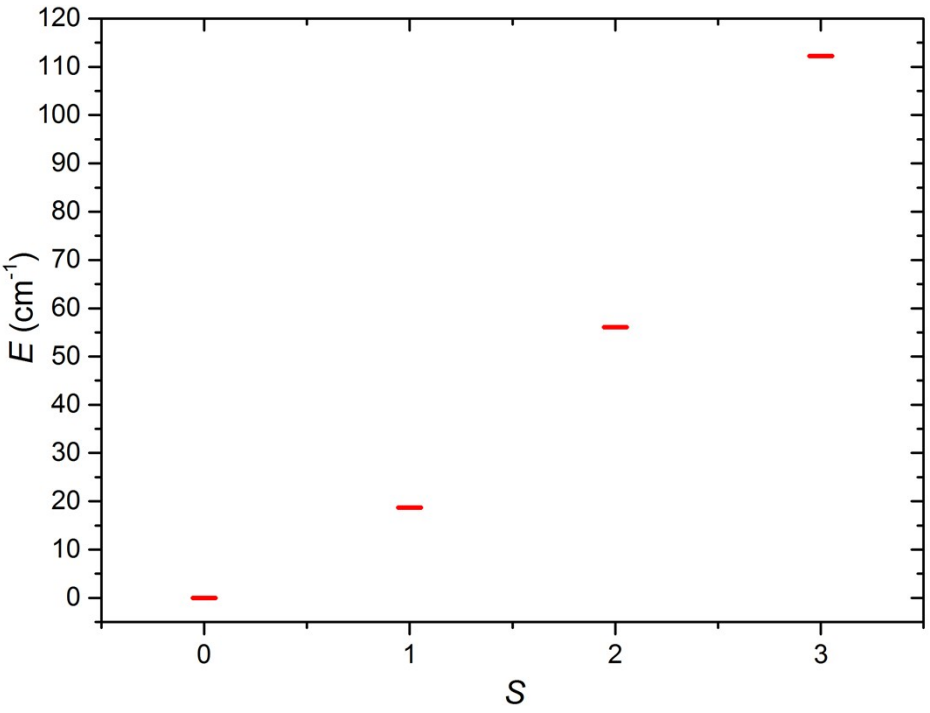

Figure S13. Energy levels of compound **7** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

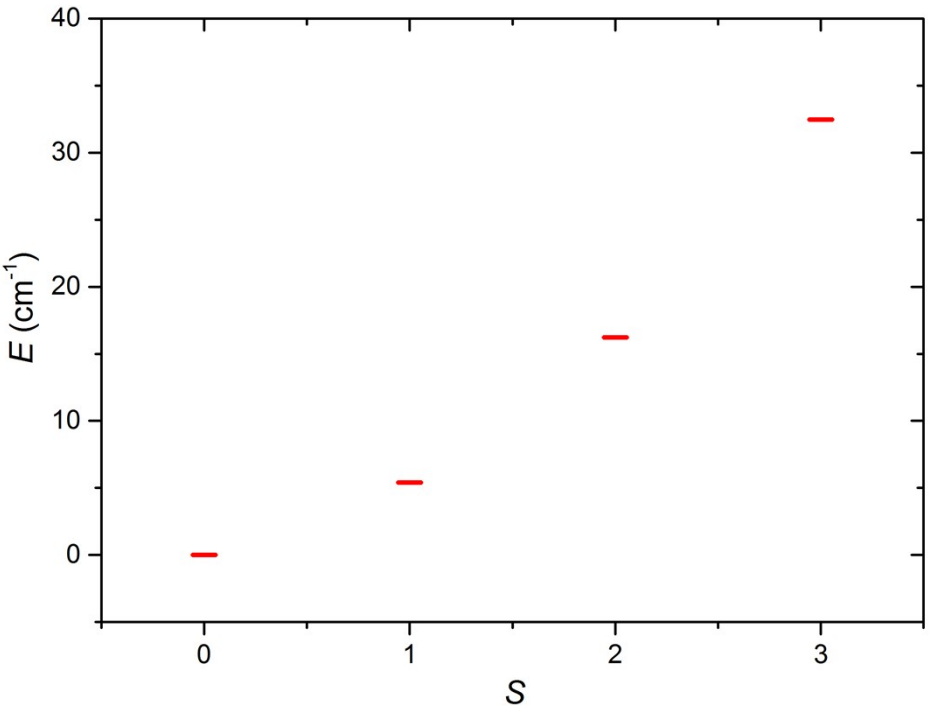

Figure S14. Energy levels of compound **8** at zero magnetic field for the isotropic spin-Hamiltonian (1) with best fit as detailed in the main text.

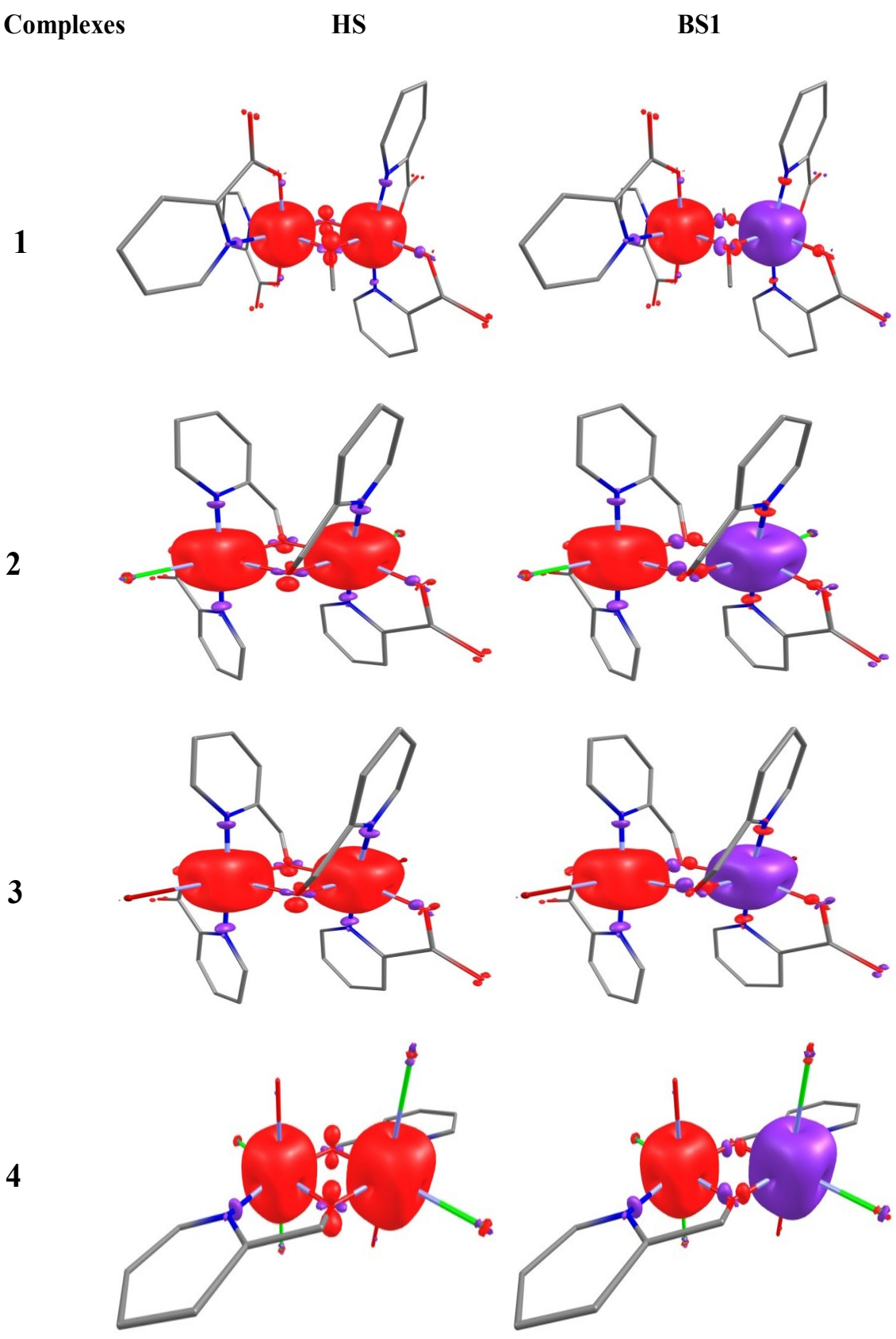

Figure S15. Spin density plots for complexes **1-4** at the UB3LYP/TZV level shown with isosurface values of 0.01 $Å^{-3}$.

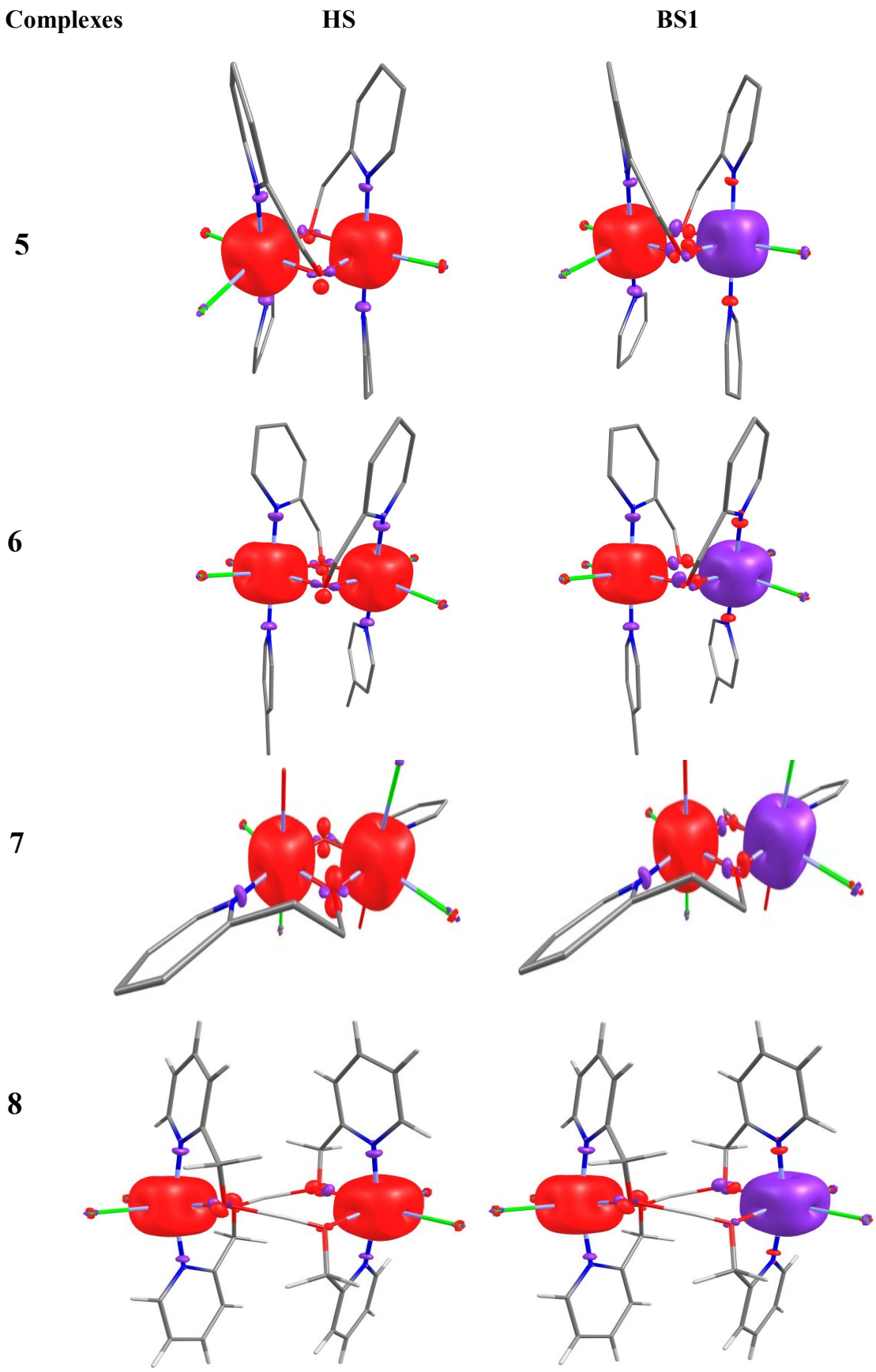

Figure S16. Spin density plots for complexes **4-8** at the UB3LYP/TZV level shown with isosurface values of 0.01 $Å^{-3}$.

Table S3. Calculated spin density values of complexes **1-8** at the UB3LYP/TZV level.

Complexes		Cr_1 Spin	Cr_2 Spin	O_1	O_2	Total Spin
1	HS	2.994	3.008	0.017	0.006	6
	BS1	2.986	-3.000	-0.009	-0.006	0
2	HS	3.024	3.024	-0.008	-0.008	6
	BS1	3.017	-3.020	0.003	-0.003	0
3	HS	3.040	3.040	-0.007	-0.007	6
	BS1	3.032	-3.030	0.004	-0.004	0
4a	HS	2.992	2.992	0.013	0.013	6
	BS1	2.988	-2.990	0.004	-0.004	0
4b	HS	2.997	2.997	0.012	0.012	6
	BS1	2.993	-2.990	0.008	-0.008	0
5a	HS	3.021	3.021	-0.017	-0.017	6
	BS1	3.014	-3.014	0.005	-0.005	0
5b	HS	2.994	2.994	-0.007	-0.007	6
	BS1	2.988	-2.988	0.011	-0.011	0
6a	HS	3.043	3.043	-0.006	-0.006	6
	BS1	3.037	-0.037	0.004	-0.004	0
6b	HS	3.043	3.043	-0.007	-0.007	6
	BS1	3.037	-3.037	-0.005	0.005	0
7	HS	3.022	3.022	0.012	0.012	6
	BS1	3.017	-3.020	0.013	-0.013	0
8	HS	3.008	3.008	0.013 0.002	0.023 0.013	6
	BS1	3.008	-3.010	0.012 -0.002	0.002 -0.012	0

Table S4. Calculated spin density values of complex **1** by varying θ.

Complex 1 (θ).		**Cr_1 Spin**	**Cr_2 Spin**	**O_1**	**O_2**	**Total Spin**
θ = 0°	HS	2.993	3.006	0.017	0.008	6
	BS1	2.985	-2.998	-0.008	-0.006	0
θ = 4°	HS	2.986	-3.000	0.017	0.006	0
	BS1	3.024	3.024	-0.009	-0.006	6
θ = 9°	HS	2.996	3.009	0.016	0.002	6
	BS1	2.987	-3.000	-0.009	-0.006	0
θ = 14°	HS	2.998	3.011	0.014	-0.002	6
	BS1	2.988	-3.002	-0.009	-0.005	0
θ = 19°	HS	3.000	3.014	0.011	-0.006	6
	BS1	2.990	-3.005	-0.009	-0.005	0
θ = 24°	HS	3.003	3.017	0.016	0.008	6
	BS1	2.993	-3.007	-0.009	-0.005	0
θ = 29°	HS	3.006	3.020	0.004	-0.014	6
	BS1	2.995	-3.011	-0.008	-0.004	0
θ = 34°	HS	3.009	3.024	0.000	-0.018	6
	BS1	2.998	-3.014	-0.008	-0.004	0
θ = 39°	HS	3.013	3.027	-0.004	-0.022	6
	BS1	3.001	-3.017	-0.008	-0.004	0
θ = 44°	HS	3.017	3.031	-0.007	-0.025	6
	BS1	3.004	-3.021	-0.008	-0.004	0

Table S5. Overlap integral values for complex **1**.

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.003	0.067	-0.032	-0.164	-0.021
d_{yz}	0.053	-0.071	0.034	-0.074	-0.036
d_{xz}	-0.319	-0.065	-0.156	0.062	0.012
d_{z^2}	0.050	-0.105	0.176	0.120	-0.003
$d_{x^2-y^2}$	0.027	0.035	0.017	0.069	-0.405

Table S6. Overlap integral values for complex **2**.

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.049	-0.060	-0.017	0.276	-0.155
d_{yz}	0.131	-0.138	0.049	0.007	-0.042
d_{xz}	-0.138	0.239	-0.060	0.088	-0.025
d_{z^2}	0.007	0.089	0.276	-0.106	-0.177
$d_{x^2-y^2}$	-0.042	0.025	-0.155	-0.177	-0.058

Table S7. Overlap integral values for complex **3**.

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	-0.205	0.132	-0.057	-0.031	-0.019
d_{yz}	0.305	-0.273	0.089	-0.118	0.082
d_{xz}	0.079	0.070	0.035	0.245	-0.126
d_{z^2}	-0.031	0.183	0.012	-0.076	-0.118
$d_{x^2-y^2}$	-0.019	-0.087	0.018	-0.118	-0.127

Table S8. Overlap integral values for complex **4a**.

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	-0.017	-0.064	-0.119	0.169	0.001
d_{yz}	0.085	-0.032	-0.017	-0.003	-0.016
d_{xz}	0.032	-0.050	0.064	0.044	-0.027
d_{z^2}	0.003	0.044	-0.169	0.111	-0.062
$d_{x^2-y^2}$	0.016	-0.028	-0.001	-0.062	-0.250

Table S9. Overlap integral values for complex **4b**.

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.024	-0.038	-0.015	-0.127	-0.058
d_{yz}	0.033	-0.175	-0.024	-0.036	-0.117
d_{xz}	-0.175	0.119	0.038	-0.049	0.045
d_{z^2}	0.036	0.049	-0.127	0.126	-0.022
$d_{x^2-y^2}$	0.117	-0.045	-0.058	-0.022	-0.229

Table S10. Overlap integral values for complex **7**.

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.244	0.129	-0.095	-0.073	0.034
d_{yz}	0.095	0.145	-0.248	-0.006	0.001
d_{xz}	0.145	-0.061	-0.124	0.098	-0.093
d_{z^2}	-0.006	0.098	0.073	0.198	-0.034
$d_{x^2-y^2}$	0.001	-0.093	-0.034	-0.034	-0.346

Table S11. Overlap integral values for complex **8**.

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.030	-0.020	-0.023	0.036	-0.012
d_{yz}	-0.001	0.052	0.030	0.062	0.022
d_{xz}	-0.052	0.003	0.020	0.022	-0.005
d_{z^2}	0.022	0.005	-0.012	0.097	-0.072
$d_{x^2-y^2}$	0.062	-0.022	0.036	-0.051	0.097

Table S12. Overlap integral values for complex **1** (θ = 24°).

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.095	0.106	0.111	-0.164	0.026
d_{yz}	0.005	0.131	-0.012	0.069	-0.048
d_{xz}	-0.115	-0.018	0.021	0.198	-0.017
d_{z^2}	-0.035	-0.083	0.196	0.094	0.040
$d_{x^2-y^2}$	-0.035	-0.032	-0.041	-0.070	-0.398

Table S13. Overlap integral values for complex **1** (θ = 44°).

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	-0.046	-0.107	-0.035	-0.263	-0.019
d_{yz}	-0.014	-0.086	-0.033	0.054	-0.035
d_{xz}	0.101	-0.026	-0.018	0.236	0.019
d_{z^2}	-0.063	-0.082	0.223	0.045	-0.097
$d_{x^2-y^2}$	-0.023	-0.006	-0.040	-0.046	-0.356

Table S14. Overlap integral values for complex **1** (ψ = 0.9°).

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.003	0.067	-0.032	-0.164	-0.021
d_{yz}	0.053	-0.071	0.034	-0.074	-0.036
d_{xz}	-0.319	-0.065	-0.156	0.062	0.012
d_{z^2}	0.027	0.035	0.017	0.069	-0.405

$d_{x^2-y^2}$	0.050	-0.105	0.176	0.120	-0.003

Table S15. Overlap integral values for complex **1** (ψ = 17.4°).

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.015	0.158	0.019	-0.139	-0.029
d_{yz}	0.049	-0.052	0.037	-0.048	-0.079
d_{xz}	0.187	-0.074	-0.046	0.114	-0.037
d_{z^2}	-0.112	-0.049	-0.123	0.033	-0.486
$d_{x^2-y^2}$	0.002	-0.066	0.108	0.070	0.007

Table S16. Overlap integral values for complex **1** (ψ = 27.6°).

Beta → Alpha ↓	d_{yz}	d_{xz}	d_{xy}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.089	-0.041	0.026	-0.125	0.055
d_{yz}	0.049	-0.094	0.045	-0.051	-0.065
d_{xz}	0.197	-0.110	-0.095	0.091	-0.065
d_{z^2}	-0.019	-0.113	-0.216	-0.008	-0.460
$d_{x^2-y^2}$	0.075	0.063	0.085	0.018	-0.117

Table S17. Pertinent structural parameters for the di-alkoxo bridged compounds **a**-**g** from the literature. r = Cr-O bond length, ϕ = Cr-O-Cr bridging angle, θ = dihedral angle between the bridging Cr_2O_2 plane and the OR vector of the bridging group, ψ = Cr-O-Cr-O dihedral angle, and J_{exp} is the experimentally determined exchange.

	Compound	**Cr-Cr [Å]**	**r [Å]**	**ϕ [°]**	**θ [°]**	**ψ [°]**	**J_{exp} [cm^{-1}]**
a	$[Cr(acac)_2(OMe)]_2$ [ref. 66]	3.028	1.950-1.973	101.0	29.81	1.37	-4.9
b	$[Cr(tmhd)_2(OMe)]_2$ [ref. 67] (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato)	3.032	1.950-1.958	101.74	31.2	0.0	-4.45
c	$[Cr(3\text{-}Br\text{-}acac)_2(OEt)]_2$ [ref. 68]	3.027	1.949-1.953	101.8	18.3	0.0	-8.94
d	$[Cr(3\text{-}Br\text{-}acac)_2(OMe)]_2$ [ref. 68]	3.038	1.961-1.963	101.44	25.52	0.0	-5.04
e	$[Cr(3\text{-}Cl\text{-}acac)_2(OMe)]_2$ [ref. 69]	3.025	1.959	101.09	24.42	0.0	-5.04
f	$[Cr(L_1)(OMe)]_2$ [ref. 70] (L_1 = tetrahydrosalen = N,N'-bis(2-hydroxybenzyl)-1,2-ethanediamine)	3.033	1.957-1.968	101.17	4.05	0.0	-10.8
g	$[Cr(HL)_2(OMe)]_2$ [ref. 71]	3.024	1.950-1.975	100.91	27.27	1.84	-10.75

	(H_2L = 2-salicyloylhydrazono-1,3-dithiolane)						