

Computational Studies of the Magneto-structural Correlations in a Manganese Dimer with Jahn-Teller Distortions

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Experimental details

Commercial reagents and solvents were used without purification. Elemental analysis was determined by the Campbell Microanalytical Laboratory at the University of Otago.

Synthesis of the dinuclear Mn^{III} complex

The Mn^{III} dimer was serendipitously synthesised in low yield by reacting the ligand **L3** in a 1:2:2 ratio with Mn(ClO₄)₂·6H₂O and CH₃ONa in acetonitrile (~6 mL) on a 0.087 mmol scale. The solution was stirred for 30–60 minutes, filtered and then left to evaporate. Black, fine, rod-shaped crystals were isolated by slow diffusion of diethyl ether into a jar containing the complex in solution. Anal. Calc. for C₆₈H_{91.2}N_{5.2}O₂₆Cl₄Mn₂·5H₂O: C 47.01, H 5.76, N 4.19%; found: C 46.80, H 5.67, N 4.54.

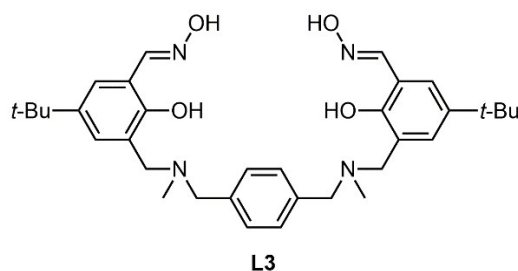


Figure S1. Structure of the di-oxime **L3**.

Charge balance

Elemental analysis was consistent with the presence of four perchlorate anions per unit complex (Table 1). Three of these were located in the crystal structure, unfortunately the fourth could not be located from the difference map, but is present within the solvent mask.

Table S1. Balance of charges for the dinuclear complex (CCDC 2124835).

Component	Charge
2 x Mn ³⁺	+ 6
2 x (L1 or L2)	0
4 x ClO ₄ ⁻	- 4
2 x OH ⁻	- 2
<i>Total</i>	<i>0</i>

X-ray crystallography

The X-ray data was collected using a Rigaku Spider diffractometer equipped with a Rigaku MM007 microfocus copper rotating anode X-ray source (CuK α , $\lambda = 1.54178 \text{ \AA}$) with high-flux Osmic monochromating and focusing multilayer mirror optics, and a curved image plate detector. The sample mounted on a MiTeGen mylar loop using Fomblin[®] oil and cooled to 153 K using an Oxford Cobra cold stream. Data was collected using Crystal Clear and processed using FS PROCESS.^{1,2} The structure was solved by intrinsic phasing with SHELXT and refined with SHELXL using full-matrix least-squares against F^2 in Olex2.³⁻⁵ Non-hydrogen atoms were refined anisotropically and hydrogen atoms were calculated to their ideal positions unless otherwise stated and refined using a riding model with fixed U_{iso} values. There exists rotational disorder on a number of *tert*-butyl groups in the structure (67:33). A solvent mask containing 149 e⁻ in 700 \AA^3 , which is consistent with the presence of 1 ClO₄⁻, 3 MeCN, and 4 H₂O (totalling 155 e⁻), was modelled using the BYPASS protocol, as implemented in Olex2.⁶

Table S2. Crystal data and structural refinement for the dinuclear Mn^{III} complex.

CCDC number	2124835
Emp. formula	C ₇₄ Cl ₄ H _{108.2} Mn ₂ N _{8.2} O ₃₀
<i>M</i> _r /g mol ⁻¹	1844.36
<i>T</i> /K	153
Space group	$\bar{1}$
Crystal system	Triclinic
<i>a</i> /Å	9.5605(2)
<i>b</i> /Å	15.8753(3)
<i>c</i> /Å	31.531(2)
α /°	92.892(7)
β /°	93.983(7)
γ /°	98.707(7)
<i>V</i> /Å ³	4710.0(4)
<i>Z</i>	2
<i>D</i> _c /g cm ⁻³	1.300
Crystal size/mm	0.45 × 0.05 × 0.04
μ /mm ⁻¹	3.882
<i>F</i> (000)	1935.0
2 θ Range /°	13.126–130.148
Reflections collected	81849
Data (<i>R</i> _{int})/restr./param.	15384(0.1032)/382/911
Goof	1.099
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.1206, 0.3141
<i>R</i> 1, <i>wR</i> 2 (<i>all data</i>)	0.1959, 0.3860
$\Delta\rho_{\max/\min}$ /e Å ⁻³	1.15/–0.83

Calculation of distortion parameters

The Δ and ρ parameters at Mn2 for each geometry were calculated with the x , y and z axes assigned for type III complexes based on Figure 4, then recalculated with the x , y and z axes reassigned for type IV. The type (III or IV) was then assigned based on the requirement that $|\Delta| > |\rho|$, if both sets of values met this standard, the Δ and ρ values with the greatest difference were selected. The values used for the calculations are presented in Tables S3 and S4. While previous publications have recommended assigning the axes such that $y > x$,⁷ the y and x axes were consistently assigned to the same atoms for each type as the $|\rho|$ values did not differ significantly depending on the assignment of these axes.

Table S3. Values for x , y and z used to calculate the elongation (Δ) and rhombicity (ρ) parameters at the Mn^{III}

Geometry	Type	Mn1					Mn2				
		x (Å)	y (Å)	z (Å)	Δ (%) ^a	ρ (%) ^a	x (Å)	y (Å)	z (Å)	Δ (%) ^a	ρ (%) ^a
1	(a) IV	3.837	3.830	4.547	18.6	-0.2	4.231	4.308	3.793	-11.2	1.8
	(b) III	3.850	3.894	4.629	19.6	1.1	3.830	4.131	4.453	11.9	7.9
	(c) III	3.842	3.912	4.584	18.2	1.8	3.892	4.060	4.465	12.3	4.3
2	(a) IV	3.837	3.830	4.547	18.6	-0.2	4.231	4.105	3.793	-9.0	-3.0
	(b) III	3.834	3.910	4.609	19.0	2.0	3.871	3.974	4.498	14.7	2.7
	(c) III	3.842	3.915	4.610	18.8	1.9	3.863	3.988	4.477	14.1	3.2
3	(a) IV	3.837	3.830	4.547	18.6	-0.2	4.109	4.308	3.793	-9.9	4.8
	(b) III	3.844	3.896	4.630	19.6	1.3	3.850	4.083	4.382	10.5	6.0
	(c) IV	3.860	3.893	4.631	19.5	0.8	4.326	4.134	3.833	-9.4	-4.4
4	(a) IV	3.837	3.830	4.547	18.6	-0.2	4.109	4.105	3.793	-7.7	-0.1
	(b) III	3.833	3.910	4.607	19.0	2.0	3.891	3.948	4.380	11.8	1.5
	(c) III	3.843	3.908	4.600	18.7	1.7	3.865	3.965	4.383	11.9	2.6

centres of the calculated geometries of 1–4.

^a Calculated from unrounded values for x , y and z .

Table S4. Values for x , y and z used to calculate the elongation (Δ) and rhombicity (ρ) parameters at the Mn^{III}

Mn–O (Å) ^a	Type	Mn1					Mn2				
		x (Å)	y (Å)	z (Å) ^b	Δ (%) ^c	ρ (%) ^c	x (Å)	y (Å)	z (Å)	Δ (%) ^c	ρ (%) ^c
1.815	IV	3.860	3.856	4.629	20.0	-0.1	4.324	4.320	3.630	-16.0	0.1
1.865	IV	3.860	3.856	4.629	20.0	-0.1	4.305	4.305	3.730	-13.4	0.0
1.915	IV	3.856	3.860	4.629	20.0	0.1	4.293	4.291	3.830	-10.8	0.0
1.965	IV	3.859	3.856	4.629	20.0	-0.1	4.286	4.283	3.930	-8.3	-0.1
2.015	III	3.833	3.884	4.629	20.0	1.3	4.030	4.040	4.478	11.0	-0.2
2.065	IV	3.857	3.856	4.629	20.0	0.0	4.339	4.320	4.130	-4.6	-0.4
2.115	IV	3.858	3.856	4.629	20.0	0.0	4.388	4.376	4.230	-3.5	-0.3

centres of the constrained geometries of the Mn^{III} dimer.

^a Constrained Mn2–O7 and Mn2–O8 bond lengths. ^b The Mn1–O1 and Mn1–O2 bond lengths were constrained to the same values for all complexes. ^c Calculated from unrounded values for x , y and z .

Unrestricted Corresponding Orbitals

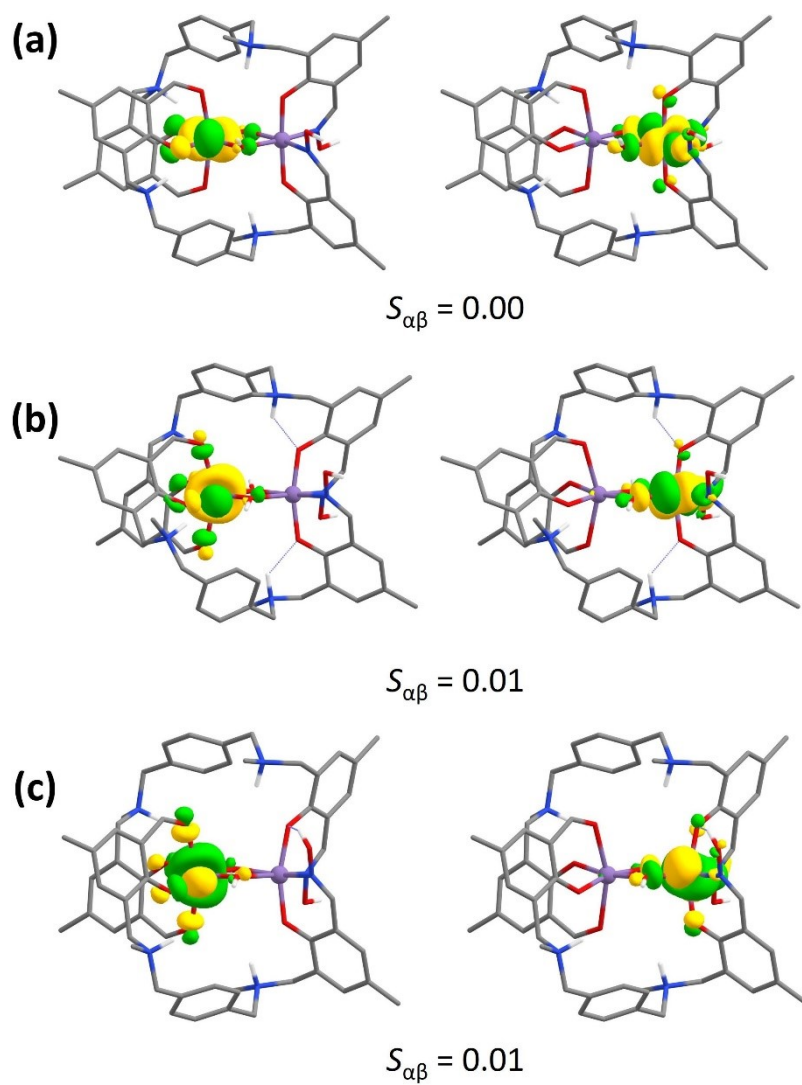


Figure S2. Magnetic orbital pair 285 α/β for geometries **1(a)–(c)**.

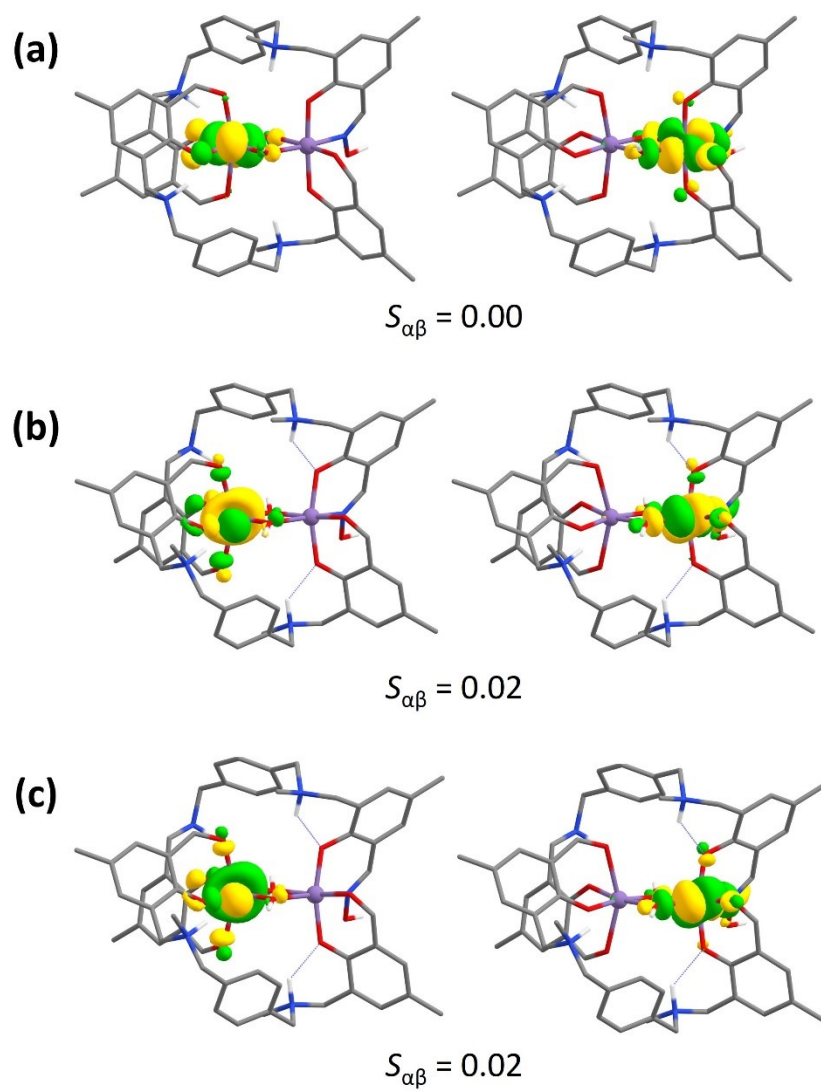


Figure S3. Magnetic orbital pair 281 α/β for geometries **2(a)**–**(c)**.

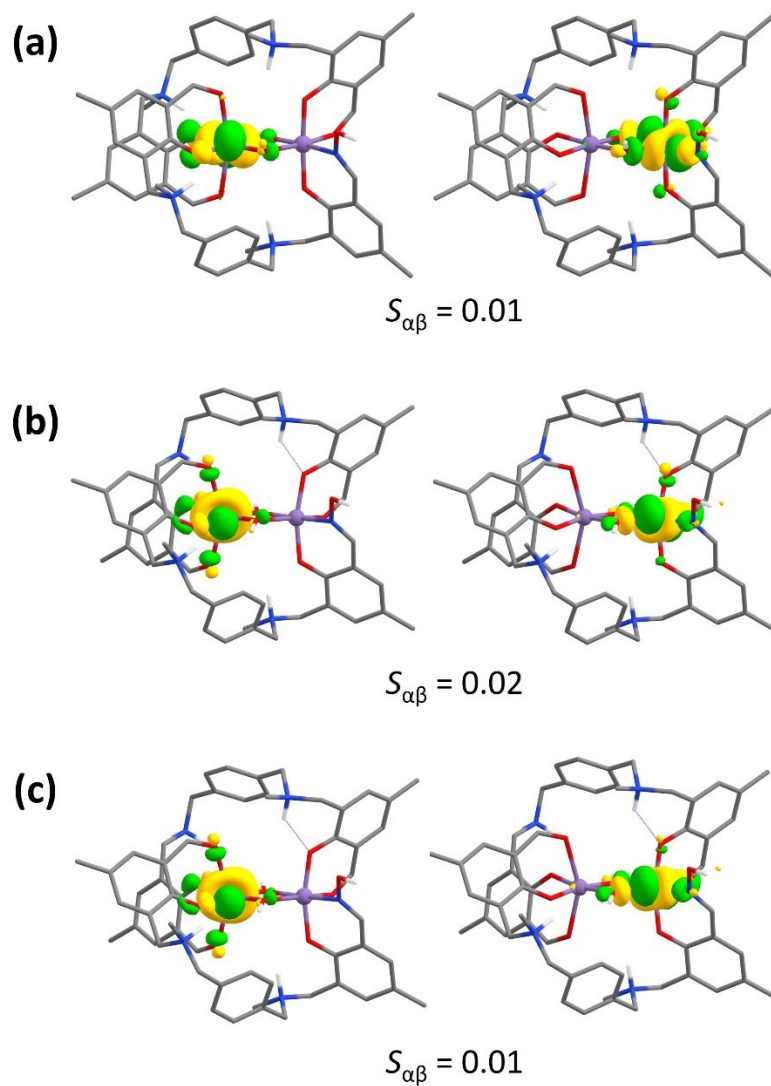


Figure S4. Magnetic orbital pair 281 α/β for geometries 3(a)–(c).

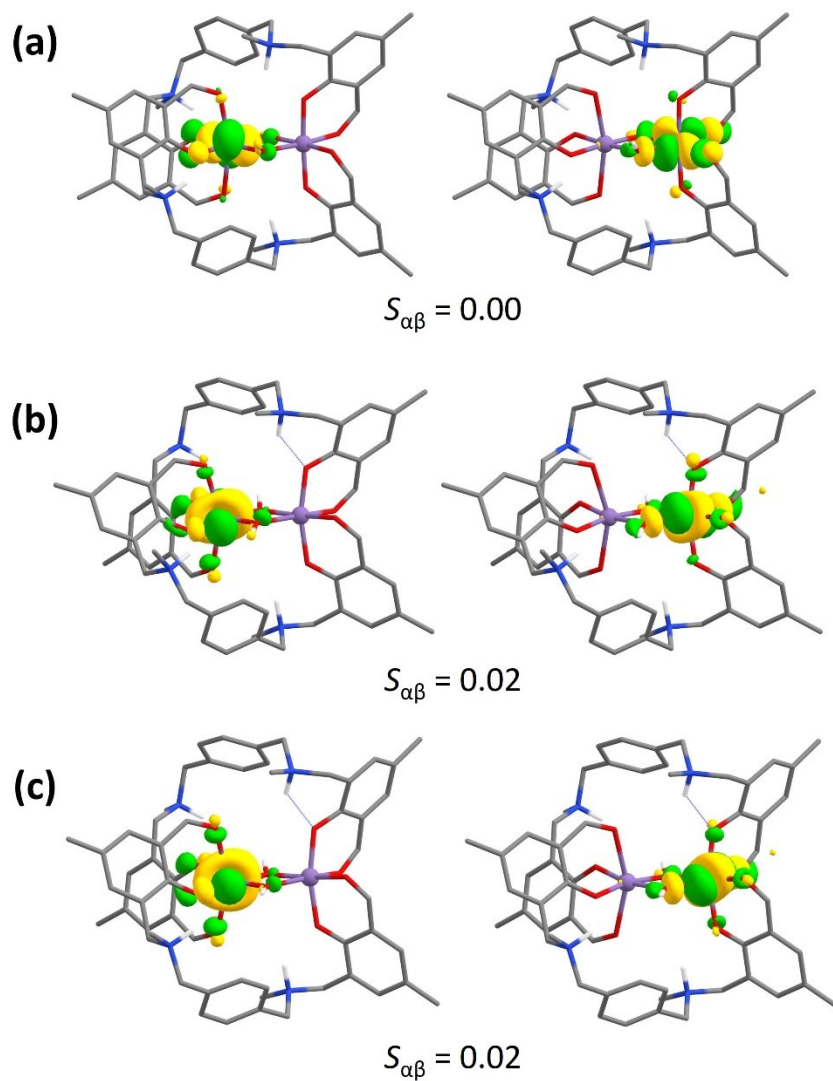


Figure S5. Magnetic orbital pair 274 α/β for geometries 4(a)–(c).

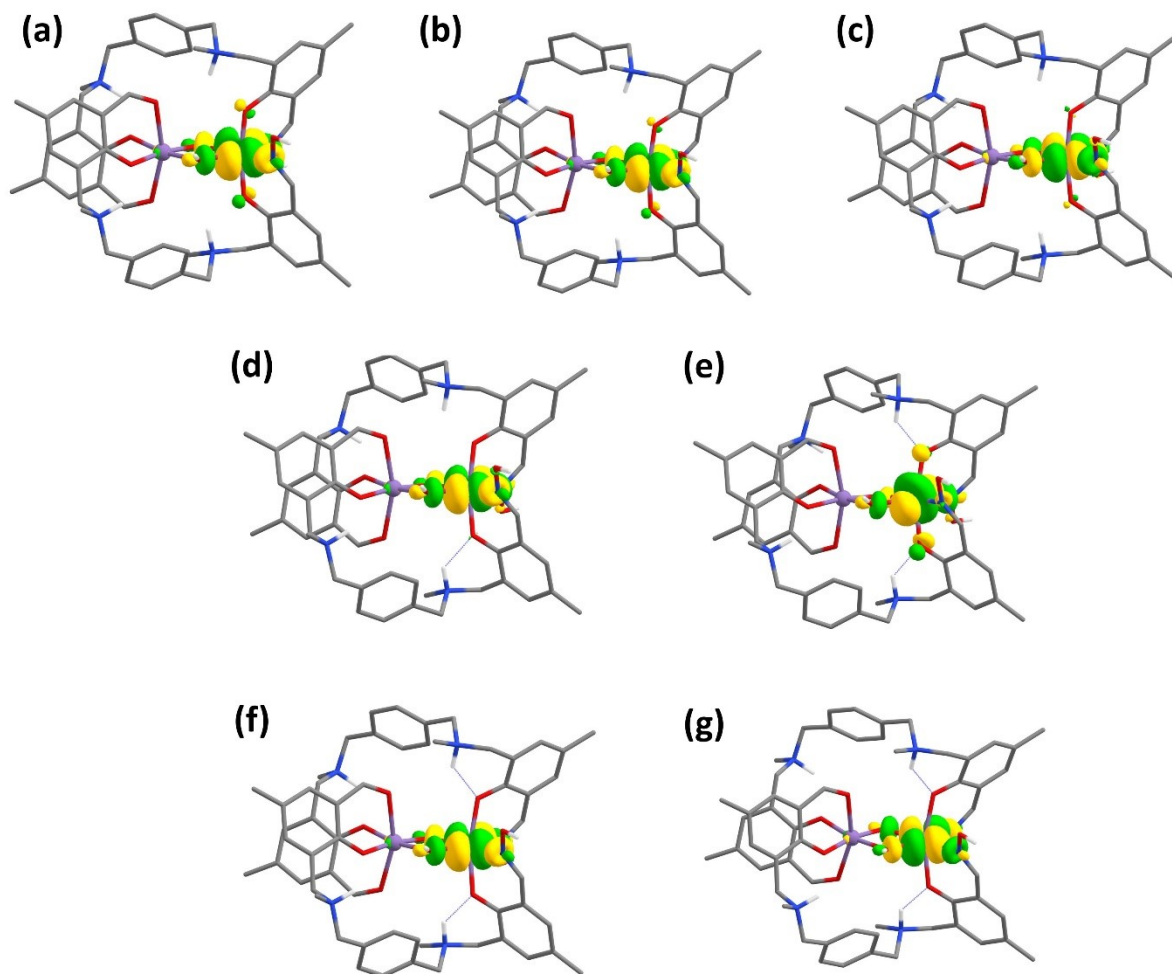


Figure S6. Magnetic orbital 285α for the constrained geometries with Mn–O_{phenolate} bond lengths constrained to (a) 1.815 Å, (b) 1.865 Å, (c) 1.915 Å, (d) 1.965 Å, (e) 2.015 Å, (f) 2.065 Å, (g) 2.115 Å.

Spin Density

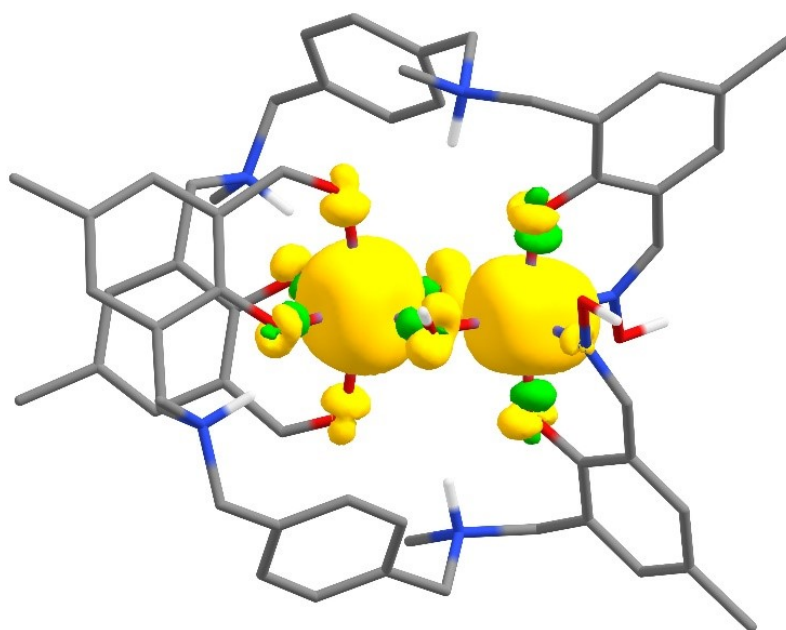


Figure S7. Spin density plot for **1(a)**.

References

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