Supplementary Materials

DFT Investigation of the Molecular Properties of the Dimethylglyoximato Complexes [M(Hdmg)$_2$] (M = Ni, Pd, Pt)

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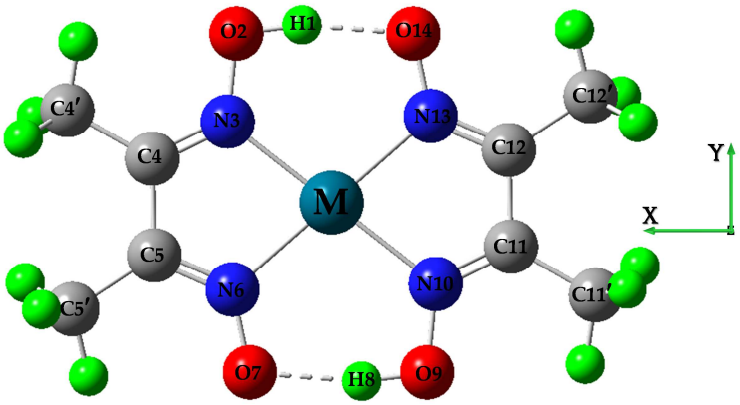
Table S1. Essential experimental structural parameters of [M(Hdmg)$_2$] (M = Ni, Pd, Pt) [a].

	O–H···O distance	O···O distance	O–H···O angle	M···M distance	rotation angle	Reference
	/Å	/ Å	/ °	/ Å	/ ° [b]	
Ni [c]	-	2.40(2)	-	3.245(3)	92.48(1)	Ref. 1
	1.354(2)	2.457(4)	172.07(2)	3.237(1)	92.59(1)	Ref. 2
	-	2.44(2)	-	3.245(5)	90(1)	Ref. 3
Pd	-	2.59(3)	-	3.26(4)	90(3)	Ref. 1
	1.889(1)	2.626(4)	166.84(1)	3.250(3)	93.46(1)	Ref. 4
Pt	1.619(15)	2.638(19)	159(13)	3.259(1)	92.9(7)	Ref. 5
	1.574(1)	2.62(2)	179.41(1)	3.256(3)	92.16(1)	Ref. 4
	-	3.03(6)	-	3.23(1)	90.34(1)	Ref. 6

[a] Experimental data from solid state structures. [b] Rotation of the square planar complexes within the stacks. [c] Values for Ni···Ni range from 3.25 to 2.90 upon pressure [7].



Numbering scheme for the DFT-calculated structures of [M(Hdmg)$_2$] (M = Ni, Pd, Pt) for Tables S2 to S4.

Table S2. Selected experimental and computed geometries of [Ni(Hdmg)$_2$] [a].

Bond length / Å	Exp. 1	Exp. 2	Exp. 3	Calc. 1	Calc. 2	Our results
M–N$_3$	1.85(1)	1.90(1)	1.861(3)	1.89	1.873	1.912
M–N$_6$	1.85(1)	1.87(2)	1.859(3)	1.90	1.894	1.912
N$_3$–O$_2$	1.36(2)	1.38(2)	1.350(4)	1.34	1.338	1.345
N$_6$–O$_7$	1.35(2)	1.37(3)	1.341(4)	1.29	1.288	1.303
O$_2$–H$_1$	-	-	1.109(3)	1.04	1.050	1.054
O$_2$···O$_{14}$	2.40(2)	2.44(2)	2.457(4)	2.49	2.477	2.509
H$_1$···O$_{14}$	-	-	1.354(2)	1.47	1.442	1.455
N$_3$–C$_4$	1.30(2)	1.20(3)	1.292(5)	1.30	1.294	1.280
C$_4$–C$_5$	1.54(3)	1.53(3)	1.467(5)	1.47	1.462	1.486
C$_5$–N$_6$	1.29(2)	1.25(3)	1.292(4)	1.30	1.305	1.289
C$_4$–C$_4$′	1.50(3)	1.46(4)	1.489(5)	1.49	1.487	1.487
C$_5$–C$_5$′	1.53(3)	1.51(4)	1.481(5)	1.49	1.486	1.489
Angles / °	**Exp. 1**	**Exp. 2** [b]	**Exp. 3**	**Calc. 1** [c]	**Calc. 2**	**Our results**
N$_3$–M–N$_6$	83.1(1)	80	82.4(1)	-	83.0	82.4
N$_6$–M–N$_{10}$	96.9(1)	100	97.6(1)	-	97.0	97.3
M–N$_3$–C$_4$	118.0(1)	121	116.3(2)	-	115.4	115.2
M–N$_6$–C$_5$	117.4(1)	117	116.6(2)	-	114.8	114.9
N$_3$–O$_2$–H$_1$	-	102	101.5(2)	-	103.3	102.7
C$_4$–N$_3$–O$_2$	117.5(1)	121	119.9(3)	-	120.3	121.3
C$_5$–N$_6$–O$_7$	119.7(1)	121	119.5(3)	-	121.7	122.5
O$_2$–H$_1$···O$_{14}$	-	-	172.1(18)	-	167.0	169.7
N$_{13}$–O$_{14}$···H$_1$	-	98	101.1(2)	-	104.3	102.6
C$_5$–C$_4$–N$_3$	110.0(1)	109	112.5(3)	-	113.5	113.8
C$_4$–C$_5$–N$_6$	111.5(1)	113	112.2(3)	-	113.3	113.7
C$_5$–C$_4$–C$_4$′	125.2(1)	124	124.3(3)	-	123.2	122.1
C$_4$–C$_5$–C$_5$′	124.0(1)	121	125.0(3)	-	125.5	124.1

[a] Exp. 1: experimental data from Ref. 1. Exp.2: experiment data from Ref. 3. Exp.3: experimental data from Ref. 2. Calc. 1: calculated data from Ref. 8. Calc. 2: calculated data from Ref. 9. Our results: solvent: DMSO(conductor-like polarizable continuum model = CPCM) Ref. 10,11; functional: M06-2X, Ref. 12; basis set: def2TZVP, Ref. 13 for C, H, N, O and LANL2DZ ecp(10/18) for Ni, Ref. 14-17. [b] No standard deviations for angles were provided. [c] No angles were provided.

Table S3. Selected experimental and computed geometries of [Pd(Hdmg)$_2$] [a].

Bond length / Å	Exp. 1	Exp. 2	Calc.	Our results
M–N_3	1.93(2)	1.967(3)	1.989	2.016
M–N_6	1.99(2)	1.962(4)	2.000	2.014
N_3–O_2	1.37(3)	1.353(1)	1.349	1.352
N_6–O_7	1.33(3)	1.321(1)	1.275	1.288
O_2–H_1	-	0.752(1)	1.014	1.009
O_2···O_{14}	2.59(3)	2.626(4)	2.669	2.713
H_1···O_{14}	-	1.889(1)	1.671	1.704
N_3–C_4	1.31(3)	1.281(1)	1.295	1.281
C_4–C_5	1.47(4)	1.472(1)	1.467	1.485
C_5–N_6	1.31(3)	1.299(1)	1.314	1.297
C_4–C_4'	1.55(4)	1.489(1)	1.489	1.489
C_5–C_5'	1.54(4)	1.486(1)	1.489	1.491
Angles / °	**Exp. 1**	**Exp. 2**	**Calc.**	**Our results**
N_3–M–N_6	80.4(1)	79.9(1)	80.0	79.4
N_6–M–N_{10}	99.6(1)	100.2(1)	100.0	100.6
M–N_3–C_4	116.6(1)	116.3(2)	115.6	115.5
M–N_6–C_5	115.1(1)	115.7(2)	114.8	115.0
N_3–O_2–H_1	-	106.7(1)	103.4	103.2
C_4–N_3–O_2	120.9(1)	121.8(3)	121.6	122.0
C_5–N_6–O_7	124.2(1)	123.0(3)	125.2	125.5
O_2–H_1···O_{14}	-	166.8(1)	167.3	168.0
N_{13}–O_{14}···H_1	-	103.2(1)	106.3	106.4
C_5–C_4–N_3	114.2(1)	114.1(3)	115.1	115.1
C_4–C_5–N_6	113.7(1)	114.0(3)	114.6	114.9
C_5–C_4–C_4'	122.5(1)	123.5(3)	122.2	121.1
C_4–C_5–C_5'	125.3(1)	124.7(3)	123.6	122.0

[a] Exp.1: experimental data from Ref. 1. Exp.2: experimental data from Ref. 4. Calc.1: calculated data from Ref. 9. Our results: solvent: DMSO(CPCM), Ref 10,11; functional: M06-2X, Ref. 12; basis set: def2TZVP, Ref. 13 for C, H, N, O and LANL2DZ ecp(28/28) for Pd, Ref. 14-17.

Table S4. Selected (experimental and computed) geometries of [Pt(Hdmg)$_2$] [a].

Bond length / Å	Exp. 1	Exp. 2	Calc. 1	Calc. 2	Our results
M–N_3	1.98(1)	1.97(2)	1.984	1.976	1.994
M–N_6	1.99(1)	1.95(2)	2.002	1.994	2.002
N_3–O_2	1.35(2)	1.34(2)	1.347	1.351	1.353
N_6–O_7	1.35(2)	1.37(2)	1.277	1.279	1.288
O_2–H_1	1.06(1)	1.04(1)	1.014	1.014	1.013
O_2···O_{14}	2.64(2)	2.62(2)	2.661	2.666	2.682
H_1···O_{14}	1.63(1)	1.57(1)	1.660	1.667	1.669
N_3–C_4	1.28 (3)	1.30(2)	1.299	1.299	1.285
C_4–C_5	1.42(3)	1.46(3)	1.464	1.461	1.479
C_5–N_6	1.31(2)	1.31(2)	1.318	1.316	1.299
C_4–C_4'	1.51(3)	1.50(3)	1.490	1.487	1.487
C_5–C_5'	1.47(3)	1.51(3)	1.490	1.487	1.489
Angles / °	**Exp. 1**	**Exp. 2**	**Calc. 1**	**Calc. 2**	**Our results**
N_3–M–N_6	78.2(5)	78.2(7)	79.6	79.5	79.0
N_6–M–N_{10}	101.8(7)	101.8(7)	100.4	100.5	101.0

M–N_3–C_4	116.8(1)	118.0(1)	116.1	116.4	116.6
M–N_6–C_5	115.9(1)	119.0(1)	115.1	115.4	115.9
N_3–O_2–H_1	111.9(8)	101.2(1)	103.4	103.6	103.6
C_4–N_3–O_2	123.2(1)	121.0(2)	121.8	121.1	121.8
C_5–N_6–O_7	125.0(1)	123.0(2)	125.0	124.6	123.9
O_2–H_1···O_{14}	159.0(1)	179.4(1)	168.7	167.4	168.9
N_{13}–O_{14}···H_1	108.0(5)	97.4(1)	105.6	106.0	105.6
C_5–C_4–N_3	115.3(2)	114.0(2)	114.9	114.6	114.3
C_4–C_5–N_6	113.9(2)	112.0(2)	114.2	114.0	114.2
C_5–C_4–C_4'	124.1(2)	123.0(2)	122.4	122.8	122.3
C_4–C_5–C_5'	126.6(2)	127.0(2)	123.8	124.1	124.6

[a] Exp. 1: experimental data from Ref. 5. Exp. 2: experimental data from Ref. 4. Calc. 1: calculated data from Ref. 18. Calc. 2: calculated data from Ref. 9. Our results: solvent: DMSO(CPCM), Ref 10,11; functional: M06-2X, Ref. 12; basis set: def2TZVP, Ref. 13 for C, H, N, O and LANL2DZ ecp(60/18) for Pt, Ref. 14-17.

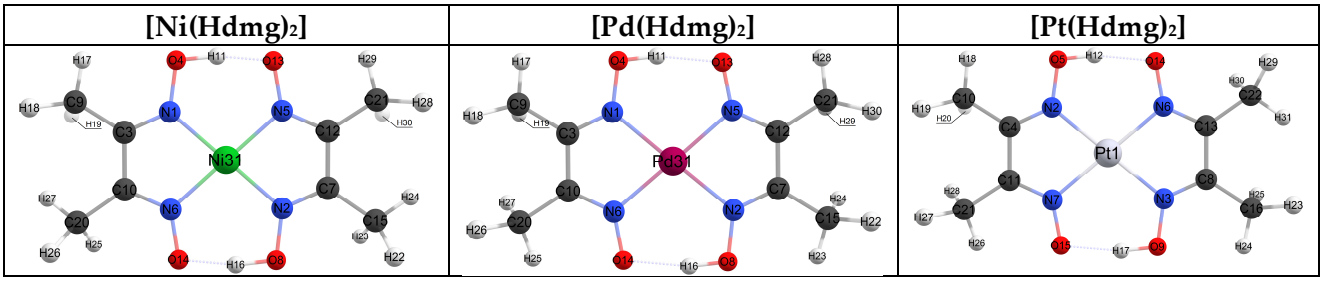


Figure S1. The optimised structures in the S_0 ground state for [M(Hdmg)$_2$] (M = Ni, Pd, Pt); M06-2X/def2TZVP/LANL2DZ ecp/CPCM(DMSO) level of theory. Note that the number refers to Table S5 and is different from Tables S2 to S4.

Table S5. The XYZ coordinates of the optimised ground state for [M(Hdmg)$_2$] (M = Ni, Pd, Pt); M06-2X/def2TZVP/LANL2DZ ecp/CPCM(DMSO) level of theory.[a]

[Ni(Hdmg)2]				[Pd(Hdmg)2]				[Pt(Hdmg)2]			
Atom	Coordinates (Å)			Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	X	Y	Z		X	Y	Z		X	Y	Z
N1	1.451518	-1.2544	-0.00187	N1	1.567954	1.26643	-0.00733	Pt1	-0.00131	-0.00131	-0.00052
N2	-1.44124	1.235723	-0.00061	N2	-1.56904	-1.26677	0.007378	N2	1.546623	1.255674	-0.00303
C3	2.619085	-0.73027	-0.00349	C3	2.724358	0.714635	-0.00374	N3	-1.54998	-1.25787	0.004221
O4	1.284163	-2.58923	-0.0046	O4	1.4159	2.610199	-0.00339	C4	2.715608	0.724064	-0.00072
N5	-1.43623	-1.2833	0.003468	N5	-1.53095	1.307239	-0.00443	O5	1.376758	2.598443	0.003515
N6	1.425195	1.26529	0.003899	N6	1.532053	-1.30762	0.004354	N6	-1.53498	1.282633	-0.00403
C7	-2.61228	0.721404	-0.00314	C7	-2.72494	-0.71395	0.003646	N7	1.534116	-1.29172	-0.00096
O8	-1.28931	2.57126	-0.00524	O8	-1.41908	-2.61093	0.003255	C8	-2.72122	-0.72882	0.003316
C9	3.884306	-1.51149	-0.00487	C9	4.004451	1.474343	0.005423	O9	-1.37359	-2.59957	0.006814
C10	2.608979	0.755579	-0.00303	C10	2.712713	-0.77064	0.002608	C10	3.979546	1.506921	0.010008
H11	0.235578	-2.69071	0.00228	H11	0.414086	2.727944	-0.00762	C11	2.717368	-0.75585	0.001526
C12	-2.61718	-0.76468	0.000975	C12	-2.71201	0.771422	-0.00248	H12	0.373978	2.711332	-0.00482
O13	-1.21376	-2.56836	0.008749	O13	-1.283	2.570877	0.00067	C13	-2.71997	0.750672	-0.00092
O14	1.216801	2.551137	0.016365	O14	1.285234	-2.5713	-0.00051	O14	-1.31691	2.552487	-0.00803
C15	-3.84483	1.555307	-0.00999	C15	-4.00574	-1.47244	-0.00584	O15	1.2964	-2.56009	-0.0103
H16	-0.24544	2.684373	0.003257	H16	-0.41824	-2.73013	0.007507	C16	-3.97894	-1.52242	0.005615
H17	3.674434	-2.57484	0.051726	H17	3.828939	2.527305	-0.1924	H17	-0.36644	-2.70667	0.00206
H18	4.505049	-1.21473	0.841846	H18	4.685469	1.066087	-0.74113	H18	3.785761	2.556075	-0.19077
H19	4.44871	-1.30209	-0.9154	H19	4.484305	1.36953	0.98079	H19	4.669223	1.108807	-0.73412
C20	3.835291	1.599349	-0.00369	C20	3.971027	-1.57019	-0.00402	H20	4.458947	1.412934	0.986775
C21	-3.8738	-1.56252	0.002429	C21	-3.9696	1.57208	0.004833	C21	3.974311	-1.55414	-0.00368
H22	-3.84635	2.21198	0.861132	H22	-4.48554	-1.36647	-0.98112	C22	-3.94536	1.596229	-0.00143
H23	-3.84991	2.192358	-0.89572	H23	-3.83126	-2.52569	0.191277	H23	-4.57416	-1.27445	-0.87445

H24	-4.74122	0.942923	-0.00191	H24	-4.68633	-1.06404	0.741032	H24	-3.76123	-2.58567	0.006515
H25	3.734931	2.38522	-0.75269	H25	3.740252	-2.60307	0.24446	H25	-4.57224	-1.27266	0.886497
H26	3.958724	2.088501	0.965174	H26	4.443788	-1.54643	-0.9886	H26	3.747612	-2.58225	0.267405
H27	4.72499	1.011823	-0.21415	H27	4.686775	-1.17581	0.717457	H27	4.435846	-1.55022	-0.9939
H28	-4.4789	-1.32874	0.880321	H28	-3.73805	2.604831	-0.24338	H28	4.697056	-1.14466	0.70205
H29	-3.62758	-2.62043	0.009637	H29	-4.44195	1.548339	0.9896	H29	-3.9523	2.243195	-0.88043
H30	-4.47344	-1.33938	-0.88193	H30	-4.68599	1.17858	-0.71647	H30	-3.95232	2.244224	0.876864
Ni31	0.000181	-0.01014	0.001386	Pd31	0.00021	-0.00061	-8.7E-05	H31	-4.84767	0.990851	-0.00096

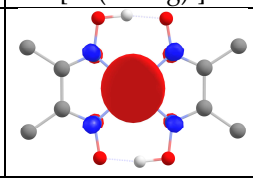
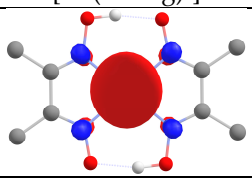
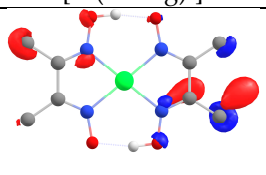
[a] Atom numbering as in Figure S1.

Table S6. Compositions (%) of frontier MOs in the S_0 ground state for [M(Hdmg)$_2$] (M = Ni, Pd, Pt) [a].

[M(Hdmg)$_2$]	MO	Energy (eV)	Component (%)	
			M	Hdmg$^-$
[Ni(Hdmg)$_2$]	LUMO+12	3.369	0	100
	LUMO+11	3.138	1	99
	LUMO+10	3.003	0	100
	LUMO+9	2.450	3	97
	LUMO+8	2.350	0	100
	LUMO+7	2.258	1	99
	LUMO+6	1.091	12	88
	LUMO+5	0.750	17	83
	LUMO+4	0.695	30	70
	LUMO+3	0.558	95	5
	LUMO+2	0.057	45	55
	LUMO+1	-0.469	3	97
	LUMO	-1.290	9	91
	HOMO	-7.592	0	100
	HOMO-1	-7.753	4	96
	HOMO-2	-8.623	1	99
	HOMO-3	-9.270	18	82
	HOMO-4	-9.567	14	86
	HOMO-5	-10.018	0	100
	HOMO-6	-10.384	66	34
	HOMO-7	-10.505	2	98
	HOMO-8	-11.336	88	12
	HOMO-9	-11.533	85	15
	HOMO-10	-11.534	6	94
	HOMO-11	-11.726	47	53
	HOMO-12	-12.375	21	79
[Pd(Hdmg)$_2$]	LUMO+12	3.308	0	100
	LUMO+11	3.096	0	100
	LUMO+10	3.002	1	99
	LUMO+9	2.507	5	95
	LUMO+8	2.395	1	99
	LUMO+7	2.268	0	100
	LUMO+6	1.306	10	90
	LUMO+5	0.855	13	87
	LUMO+4	0.781	20	80
	LUMO+3	0.617	92	8
	LUMO+2	-0.087	28	72
	LUMO+1	-0.387	5	95
	LUMO	-1.242	8	92

	HOMO	-7.609	7	93
	HOMO-1	-7.655	1	99
	HOMO-2	-8.282	3	97
	HOMO-3	-8.896	58	42
	HOMO-4	-9.419	45	55
	HOMO-5	-9.937	53	47
	HOMO-6	-10.146	0	100
	HOMO-7	-10.453	88	12
	HOMO-8	-10.506	3	97
	HOMO-9	-10.987	70	30
	HOMO-10	-11.082	86	14
	HOMO-11	-11.751	1	99
	HOMO-12	-11.958	30	70
[Pt(Hdmg)$_2$]	LUMO+12	3.290	0	100
	LUMO+11	3.082	0	100
	LUMO+10	2.949	2	98
	LUMO+9	2.873	12	88
	LUMO+8	2.387	1	99
	LUMO+7	2.144	0	100
	LUMO+6	1.596	5	95
	LUMO+5	1.251	21	79
	LUMO+4	1.015	10	90
	LUMO+3	0.911	18	82
	LUMO+2	0.732	90	10
	LUMO+1	-0.327	9	91
	LUMO	-1.480	6	94
	HOMO	-7.542	18	82
	HOMO-1	-7.735	0	100
	HOMO-2	-8.522	3	97
	HOMO-3	-8.794	84	16
	HOMO-4	-9.004	63	37
	HOMO-5	-9.691	47	53
	HOMO-6	-9.822	84	16
	HOMO-7	-10.234	0	100
	HOMO-8	-10.589	77	23
	HOMO-9	-10.784	5	95
	HOMO-10	-10.804	43	57
	HOMO-11	-11.843	2	98
	HOMO-12	-12.116	14	86

[a] Solvent: DMSO(CPCM), Ref. 10,11; functional: M06-2X, Ref. 12; basis set: For C H N O: def2TZVP, Ref. 13 and for Ni, Pd, Pt: LANL2DZ ecp, Ref. 14-17.

MO	[Ni(Hdmg)$_2$]	[Pd(Hdmg)$_2$]	[Pt(Hdmg)$_2$]
LUMO+3			

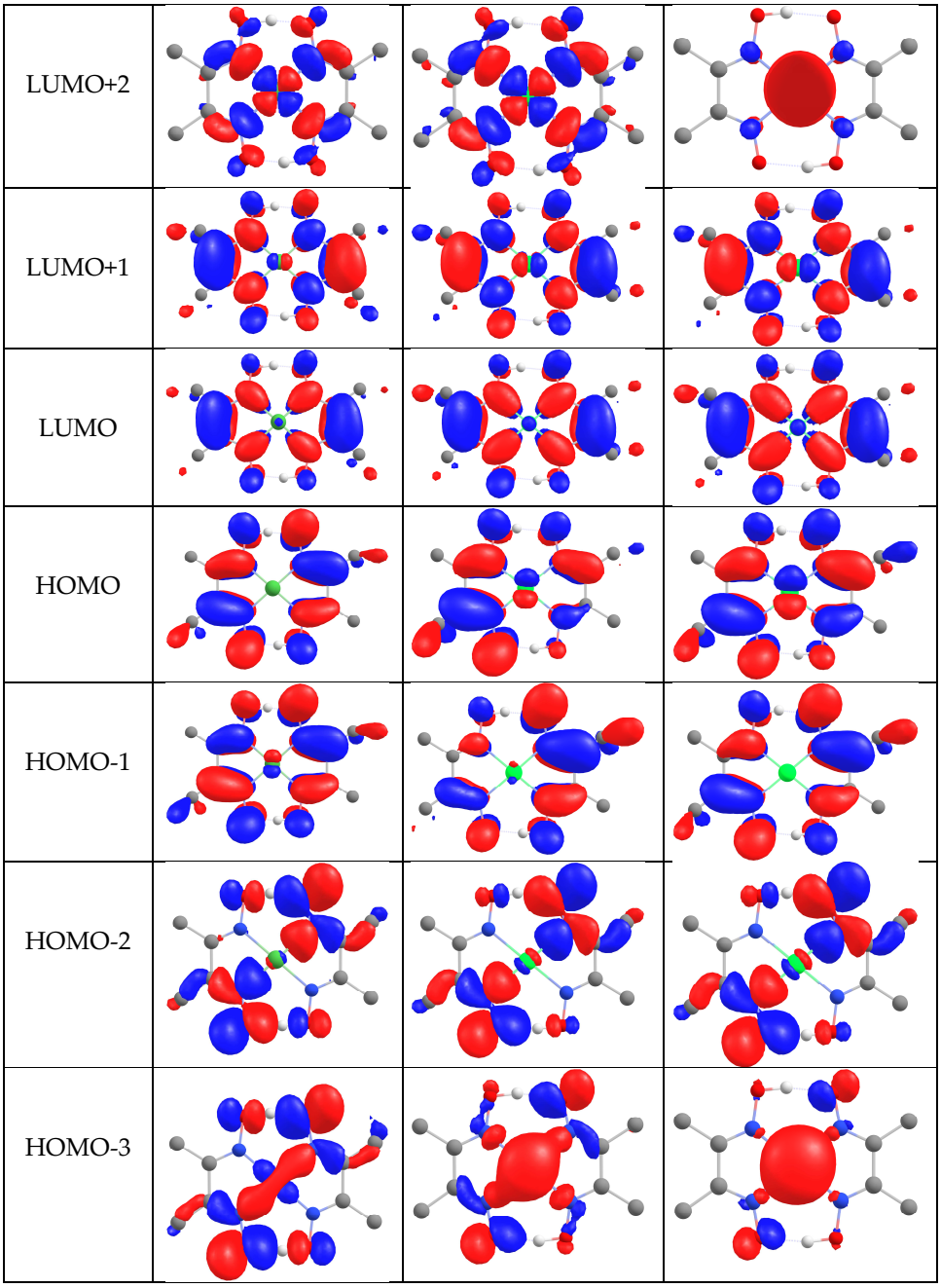


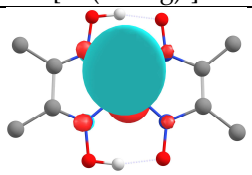
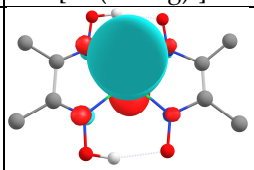
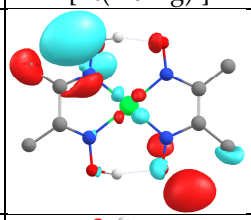
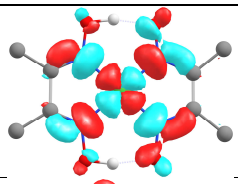
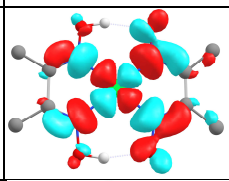
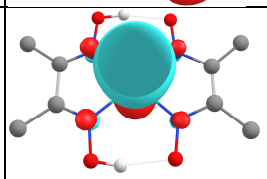
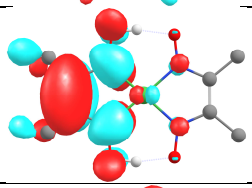
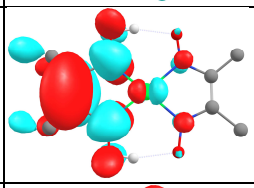
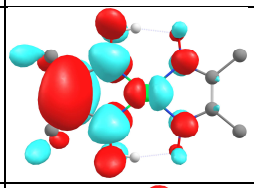
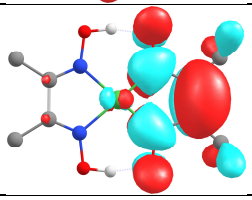
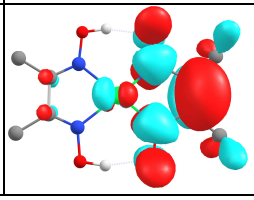
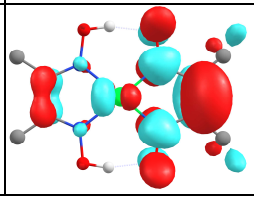
Figure S1. Frontier orbital landscape in the S_0 ground state for [M(Hdmg)$_2$] (M = Ni, Pd, Pt); M06-2X/def2TZVP/LANL2DZ ecp/CPCM(DMSO) level of theory.

Table S7. Compositions (%) of frontier MOs in the T_1 excited state for [M(Hdmg)$_2$] (M = Ni, Pd, Pt) [a].

[M(Hdmg)$_2$]	MO	Energy (eV)	Component (%)	
			M	Hdmg
[Ni(Hdmg)$_2$]	HSOMO+3	0.627	93	7
	HSOMO+2	0.504	32	68
	HSOMO+1	-1.207	5	95
	HSOMO	-5.637	5	95

	LSOMO	-7.779	6	94
	LSOMO-1	-8.601	5	95
	LSOMO-2	-9.082	7	93
	LSOMO-3	-9.171	7	93
[Pd(Hdmg)$_2$]	HSOMO+3	0.644	91	9
	HSOMO+2	0.096	26	74
	HSOMO+1	-1.215	6	94
	HSOMO	-5.470	8	92
	LSOMO	-7.618	13	87
	LSOMO-1	-8.496	36	64
	LSOMO-2	-8.798	9	91
	LSOMO-3	-9.121	7	93
[Pt(Hdmg)$_2$]	HSOMO+3	0.974	13	87
	HSOMO+2	0.731	94	6
	HSOMO+1	-1.356	12	88
	HSOMO	-5.458	10	90
	LSOMO	-7.499	26	74
	LSOMO-1	-8.710	66	34
	LSOMO-2	-8.717	13	87
	LSOMO-3	-9.173	63	37

[a] Solvent: DMSO(CPCM), Ref. 10,11; functional: M06-2X, Ref. 12; basis set: For C H N O: def2TZVP, Ref. 13, and for Ni, Pd, Pt: LANL2DZ ecp, Ref. 14-17.

MO	[Ni(Hdmg)$_2$]	[Pd(Hdmg)$_2$]	[Pt(Hdmg)$_2$]
HSOMO+3			
HSOMO+2			
HSOMO+1			
HSOMO			

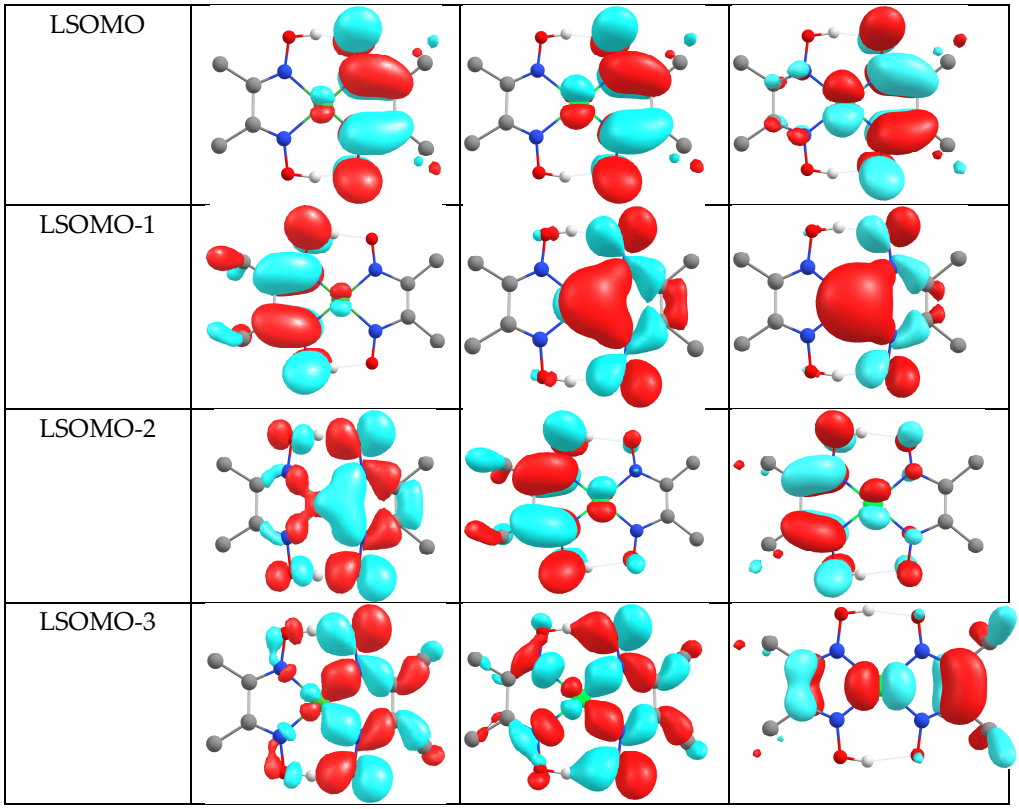


Figure S3. Frontier orbital landscape in the T_1 excited state for [M(Hdmg)$_2$] (M = Ni, Pd, Pt); M06-2X/def2TZVP/LANL2DZ ecp/CPCM(DMSO) level of theory.

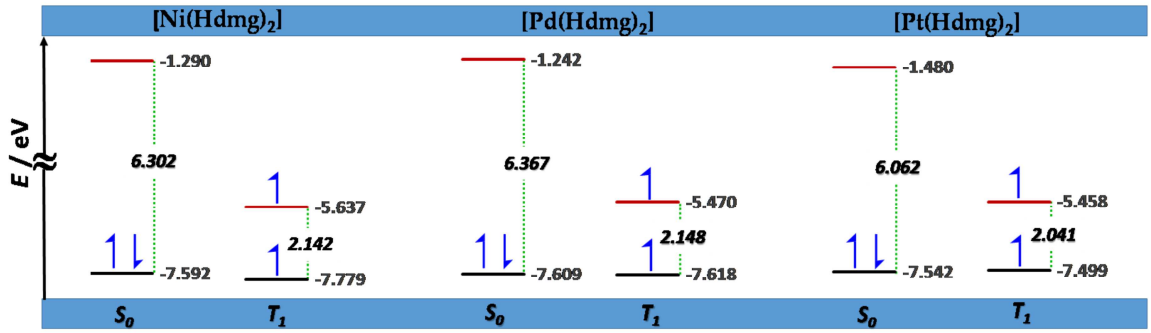


Figure S4. Energy diagrams of frontier MOs for [M(Hdmg)$_2$] (M = Ni, Pd, Pt) at the optimised S_0 and T_1 geometry; M06-2X/def2TZVP/LANL2DZ epc/CPCM(DMSO) level of theory.

Table S8. Wavelengths and character of calculated transitions for [Ni(Hdmg)$_2$] [a].

Excited state	Oscillator Strength	Calculated λ (nm)	Transitions (Major Contribution)	Assignment
$S_0 \rightarrow S_6$	0.1507	309.48	H-1→LUMO (79%)	π–π^*
			HOMO→L+1 (12%)	π–π^*
$S_0 \rightarrow S_{11}$	0.0377	247.81	HOMO→L+1 (72%)	π–π^*
			H-1→LUMO (17%)	π–π^*
$S_0 \rightarrow S_{15}$	0.3175	212.94	H-2→L+2 (67%)	π–π^*
			H-4→LUMO (14%)	π–π^*/MLCT

			HOMO→L+1 (13%)	π–π*
$S_0 \rightarrow S_{16}$	0.6855	210.74	H-4→LUMO (74%)	π–π*/MLCT
			H-2→L+2 (13%)	π–π*
$S_0 \rightarrow S_{29}$	0.0837	181.74	H-8→LUMO (77%)	MLCT/π–π*
$S_0 \rightarrow S_{32}$	0.3173	177.67	H-9→LUMO (54%)	MLCT/π–π*
			H-7→L+2 (15%)	π–π*
			H-8→LUMO (13%)	MLCT/π–π*
			H-5→L+1 (10%)	π–π*
$S_0 \rightarrow S_{39}$	0.355	171.27	H-2→L+6 (26%)	π–π*
			H-7→L+2 (19%)	π–π*
			H-9→LUMO (12%)	MLCT/π–π*
			HOMO→L+7 (10%)	π–π*
$S_0 \rightarrow S_{41}$	0.3292	169.66	H-2→L+6 (41%)	π–π*
			H-7→L+2 (12%)	π–π*
			H-3→L+5 (11%)	π–π*/MLCT
$S_0 \rightarrow S_{44}$	0.0776	165.35	H-5→L+1 (54%)	π–π*
			H-7→L+2 (18%)	π–π*

[a] Solvent: DMSO(CPCM), Ref. 10,11: functional: M06-2X, Ref. 12; basis set: For C, H, N, O: def2TZVP, Ref. 13, and for Ni: LANL2DZ ecp(10/18), Ref. 14-17; H and L are abbreviation for HOMO and LUMO, respectively.

Table S9. Wavelengths and character of calculated transitions for $[Pd(Hdmg)_2]$[a].

Excited state	Oscillator Strength	Calculated λ (nm)	Transitions (Major Contribution)	Assignment
$S_0 \rightarrow S_3$	0.0917	312.11	H-1→LUMO (48%)	π–π*
			HOMO→LUMO (35%)	π–π*
$S_0 \rightarrow S_{11}$	0.0652	238.84	HOMO→L+1 (26%)	π–π*
			H-1→L+1 (19%)	π–π*
			H-2→L+1 (17%)	π–π*
$S_0 \rightarrow S_{14}$	0.382	231.28	H-4→LUMO (82%)	π–π*/MLCT
$S_0 \rightarrow S_{20}$	0.2534	197.45	H-7→LUMO (23%)	MLCT/π–π*
			H-2→L+2 (22%)	π–π*
			H-8→L+1 (16%)	π–π*
			H-6→L+1 (10%)	π–π*
$S_0 \rightarrow S_{21}$	0.2101	196.36	H-2→L+2 (29%)	π–π*
			H-9→LUMO (22%)	MLCT/π–π*
			H-6→L+1 (16%)	π–π*
$S_0 \rightarrow S_{29}$	0.114	184.43	H-11→LUMO (23%)	π–π*
			H-7→L+1 (22%)	MLCT/π–π*
			H-9→LUMO (10%)	MLCT/π–π*
$S_0 \rightarrow S_{30}$	0.3772	184.08	H-9→LUMO (34%)	MLCT/π–π*
			H-8→L+1 (11%)	π–π*
$S_0 \rightarrow S_{38}$	0.4475	170.73	HOMO→L+7 (19%)	π–π*
			HOMO→L+8 (16%)	π–π*
			H-1→L+7 (12%)	π–π*
$S_0 \rightarrow S_{41}$	0.2158	169.09	H-6→L+2 (23%)	π–π*
			HOMO→L+6 (12%)	π–π*
			H-6→L+1 (11%)	π–π*
$S_0 \rightarrow S_{43}$	0.0936	167.29	H-3→L+3 (58%)	d–p/MLCT/π–π*
$S_0 \rightarrow S_{43}$	0.0753	165.68	H-6→L+2 (35%)	π–π*

	H-6→L+1 (17%)	π–π*
	H-2→L+6 (11%)	π–π*

[a] Solvent: DMSO, DMSO(CPCM), Ref. 10,11: functional: M06-2X, Ref. 12; basis set: For C, H, N, O: def2TZVP, Ref. 13, and for Pd,: LANL2DZ ecp(28/18), Ref. 14-17; H and L are abbreviation for HOMO and LUMO, respectively.

Table S10. Wavelengths and character of calculated transitions for [Pt(Hdmg)$_2$] [a].

Excited state	Oscillator Strength	Calculated λ (nm)	Transitions (Major Contribution)	Assignment
$S_0 \rightarrow S_1$	0.0687	349.82	HOMO→LUMO (90%)	π–π*/MLCT
$S_0 \rightarrow S_8$	0.4486	252.79	H-4→LUMO (90%)	MLCT/π–π*
$S_0 \rightarrow S_{10}$	0.2385	237.21	H-1→L+1 (74%)	π–π*
			H-6→LUMO (16%)	MLCT/π–π*
$S_0 \rightarrow S_{29}$	0.186	186.54	H-10→LUMO (77%)	π–π*/MLCT
			H-7→L+1 (13%)	π–π*
$S_0 \rightarrow S_{31}$	0.0459	180.77	H-9→L+1 (48%)	π–π*
			H-12→LUMO (16%)	π–π*/MLCT
			H-3→L+2 (15%)	d–p/MLCT/π–π*
$S_0 \rightarrow S_{32}$	0.9052	177.32	H-2→L+5 (85%)	π–π*
$S_0 \rightarrow S_{34}$	0.1484	174.91	H-3→L+2 (79%)	d–p/MLCT/π–π*
			H-9→L+1 (12%)	π–π*
$S_0 \rightarrow S_{36}$	0.468	171.43	HOMO→L+7 (58%)	π–π*/MLCT
			H-1→L+8 (21%)	π–π*
$S_0 \rightarrow S_{37}$	0.0725	171.11	H-2→L+4 (58%)	π–π*
$S_0 \rightarrow S_{44}$	0.0721	163.75	H-3→L+4 (58%)	MLCT/IL
			H-2→L+6 (22%)	π–π*

[a] Solvent: DMSO(CPCM), Ref. 10,11: functional: M06-2X, Ref. 12; basis set: For C, H, N, O: def2TZVP, Ref. 13, and for Pt: LANL2DZ ecp(60/10), Ref. 14-17; H and L are abbreviation for HOMO and LUMO, respectively.

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