Electronic supplementary information (ESI)

Glyoxalbis(2-methylmercaptoanil) complexes of nickel and ruthenium: radical versus non-radical states

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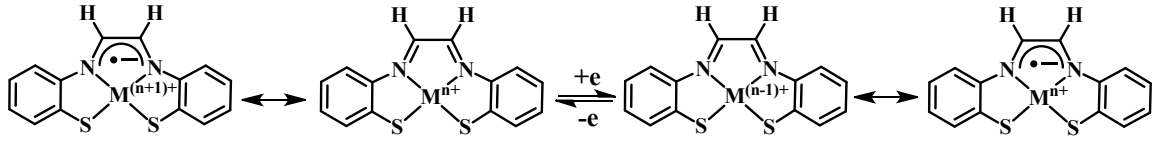

Scheme S1 Electron transfer series of gma

Table S1 Crystallographic data of gmma, **1**.CH_2Cl_2, **2** and **3**$^+Cl^-.H_2O$

	gmma	**1**.CH_2Cl_2	**2**	**3**$^+Cl^-.H_2O$
Formula	$C_{16}H_{16}N_2S_2$	$C_{16}H_{16}N_2Cl_2S_2Ni.CH_2Cl_2$	$C_{16}H_{16}Cl_2N_2S_2Ru$	$C_{34}H_{31}N_2Cl_2PS_2Ru.H_2O$
CCDC	1497586	1497587	1497588	1497589
Fw	300.65	514.96	472.40	752.68
crystal colour	Yellow	green	green	dark green
crystal system	monoclinic	orthorhombic	monoclinic	hexagonal
space group	*P2(1)/n*	*Pnma*	*P2$_1$/c*	*P6(3)/m*
a, Å	7.7926(4)	18.1597(19)	7.4899(3)	19.963(5)
b, Å	10.5057(6)	16.2161(18)	24.1677(8)	19.963(5)
c, Å	18.1128(11)	6.9479(7)	19.6549(7)	15.819(5)
β˚/γ°	92.035(3)	90	100.840(10)	120
V, Å^3	1481.90(15)	2046.0(4)	3494.3(2)	5460(3)
Z	4	4	8	6
T, K	293(2)	293(2)	296(2)	273(2)
calcd, g cm^{-3}	1.348	1.672	1.796	1.374
unique reflections	1518	2541	7164	4313
refection (I>2σ(I))	1211	2269	5031	3265
λ, Å /μ, mm-1	0.71073/0.350	0.71073/1.680	0.71073/1.433	0.71073/ 0.764
F(000)	316	1048	1888	2304
R1[a][I>2σ(I))]/ GoF[b]	0.0409/ 0.969	0.0271/ 0.971	0.0402/ 1.135	0.0532 / 1.061
R1[a] (all data)	0.0545	0.0313	0.0666	0.0704
wR2[c] (I>2σ (I))	0.1043	0.0725	0.0788	0.1523
No. of parameters	92	124	419	213
residual density, *eÅ^{-3}*	0.212	0.412	0.979	1.132

[a]R1 = $\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$. [c]wR2 = $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where w = $1/[\sigma^2(F_o^2)+(aP)^2+bP]$, P = $(F_o^2+2F_c^2)/3$.

Table S2 Redox potential data of gmma, **1**, **2**, **3**$^{+}$Cl^{-} and **4**^{PF6} in CH_2Cl_2 (0.20 M $[N(n\text{-}Bu)_4]PF_6$) at 298 K (with respect to ferrocenium^{+}/ferrocene couple)

Compounds	$E_{½}$ (V) (ΔE^c, mV)	$E_{½}$ (V) (ΔE^c, mV)
gmma	+ 0.67[a]	-1.81[b]
1	-	-0.34 (260), -0.59 (90)
2	+ 0.47 (70)	-1.22 (80)
3^{+}Cl^{-}	+0.68[a]	-0.73(100), -1.36 (200)
4^{PF6}	-	-1.28 (170)
[a]anodic peak, [b]cathodic peak, [c]peak-to-peak separation		

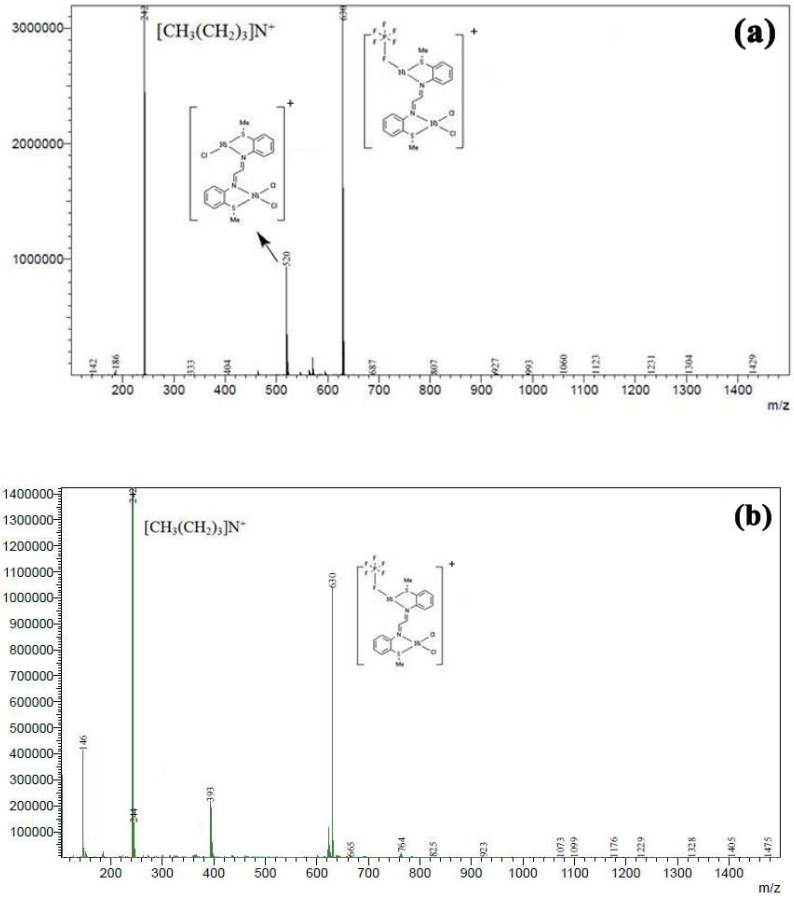

Fig. S1 ESI mass spectra of **4**^{PF6} in MeOH solvent.

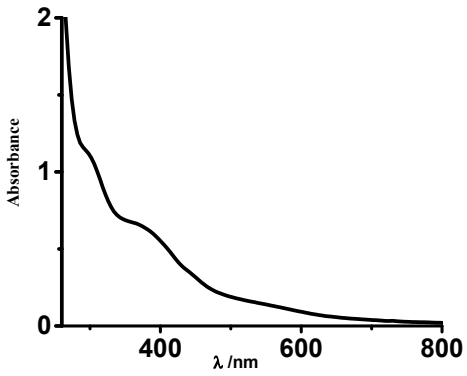

Fig. S2 UV-vis absorption of $\mathbf{4}^{PF6}$ in CH_2Cl_2 solvent.

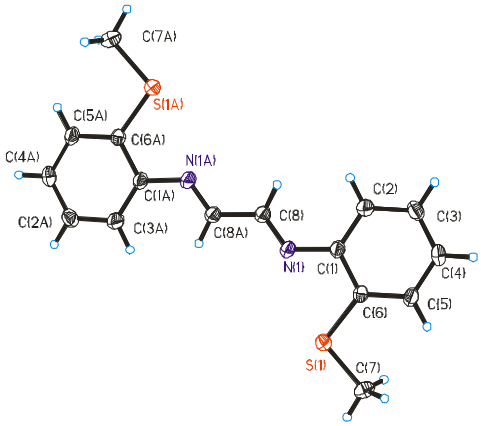

Fig. S3 Molecular geometry of gmma in crystals (40% thermal ellipsoids).

Table S3 EPR measurement parameters

complexes	Mod. Ampl. (mT)	Field Center (mT)	BO-Sweep (mT)	Frequency (GHz)	Sweep Time (s)
$\mathbf{1}^{-}$ (solution)	0.20	338.77	199.74	9.466030	30
$\mathbf{1}^{-}$ (frozen)	0.16	309.01	499.84	9.471477	60
$\mathbf{2}^{-}$ (frozen)	0.20	336.83	199.74	9.469302	60
$\mathbf{2}^{-}$ (solution)	0.20	336.83	199.74	9.465960	60
$\mathbf{2}^{+}$ (frozen)	0.50	336.83	499.64	9.44804	60
3 (solution)	0.20	337.94	199.74	9.466562	60
3 (frozen)	0.20	337.94	199.74	9.468754	60
$\mathbf{4}^{PF6-}$ (frozen)	0.20	338.50	199.74	9.470511	30

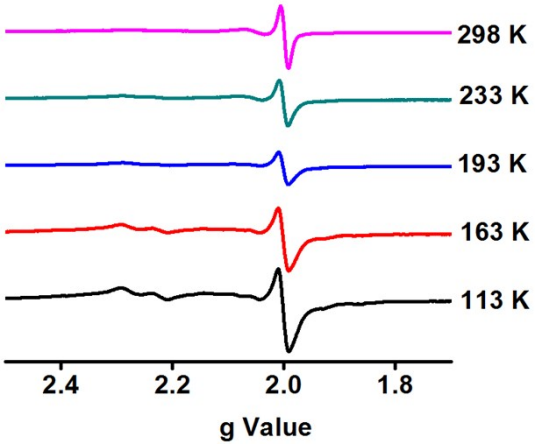

Fig. S4 Variable temperature (298-113 K) X-band EPR spectra of $\mathbf{2}^{-}$ in CH_2Cl_2 solution.

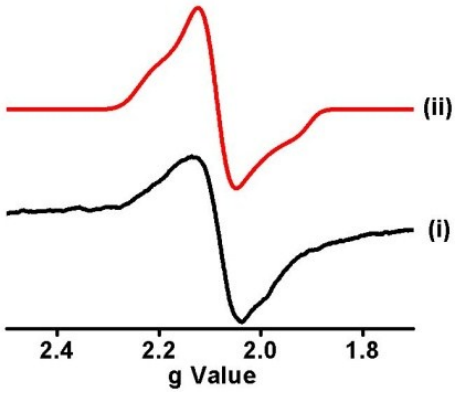

Fig. S5 X-band EPR spectra of the CH_2Cl_2 frozen glass of $\mathbf{2}^{+}$ at 113 K ((i) experimental, (ii) simulated).

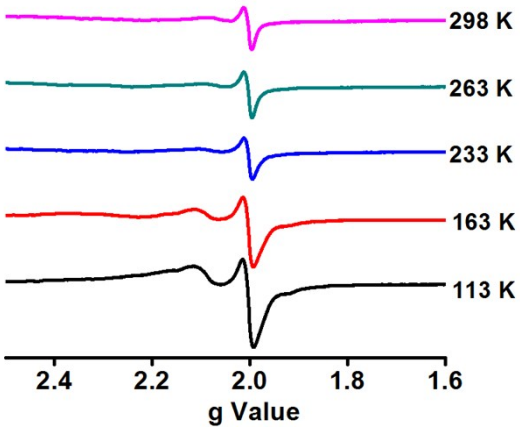

Fig. S6 Variable temperature (298-113 K) X-band EPR spectra of **3** in CH_2Cl_2 solution.

Chart S1 Optimized geometries of $\mathbf{1}^{2-}$ as (a) bis(methylthio-imine) donor and (b) NN-donor

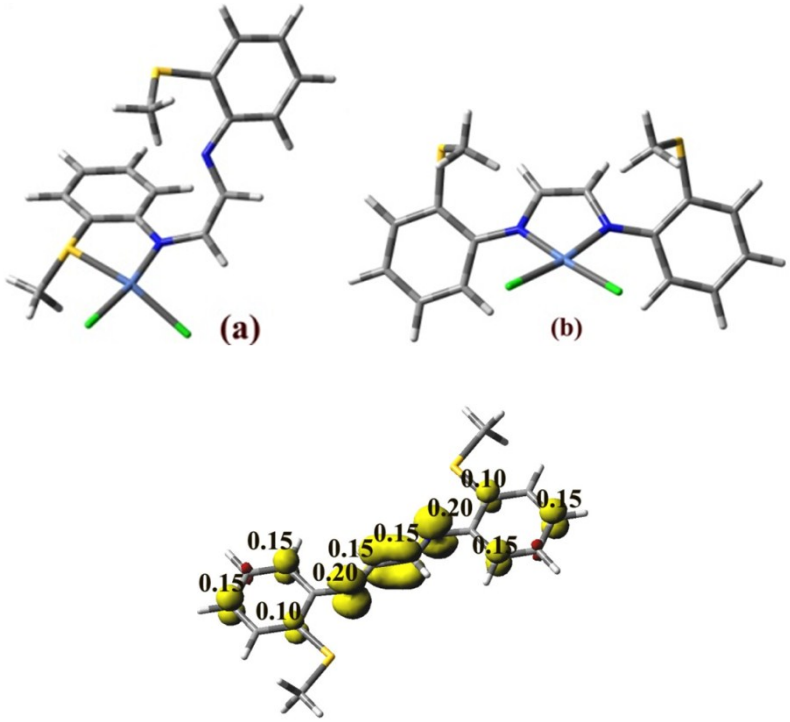

Fig. S7 Atomic spin of gmma$^{\bullet-}$.

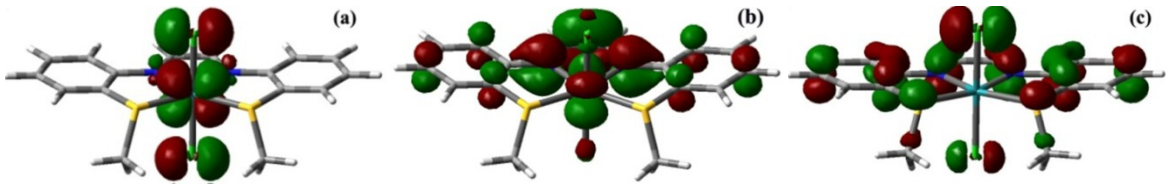

Fig. S8 Frontier molecular orbitals of **2** (a) HOMO (b) LUMO and (c) HOMO-3

Table S4 UV-vis absorption spectral data and calculated excitation energies (λ/nm), oscillation strengths (f) and transition types of gmma, **1**, **2**, $\mathbf{3}^{Me+}$ and **4** obtained from TD DFT calculations in CH_2Cl_2

λ_{exp}/nm	λ_{calc}/nm	f	significant contributions (> 12%)	transition types
gmma				
406 (0.19), 296 (0.55)	474.02	0.45	LUMO → LUMO+1 (92%)	$\pi_{aromatic} \rightarrow \pi^*$
	362.48	0.27	HOMO-2 → LUMO+1 (82%)	$\pi_{aromatic} \rightarrow \pi_{aromatic}^*$
	312.37	0.35	HOMO-4 → LUMO+1 (80%)	$\pi \rightarrow \pi_{aromatic}^*$
1				
468 (0.11), 414 (0.71), 386 (0.87) (0.51), 369 (0.82)	455.52	0.05	*β*- HOMO-2 → *β*- LUMO (65%)	$p_{Cl} \rightarrow \pi^*$
	453.32	0.21	*β*- HOMO-4 → *β*- LUMO (20%)	$p_{Cl} \rightarrow \pi^*$
			β- HOMO-2 → *β*- LUMO (20%)	$p_{Cl} \rightarrow \pi^*$
			β- HOMO → *β*- LUMO (22%)	$\pi \rightarrow \pi^*$
	443.04	0.06	*α* -HOMO-6 → *α* -LUMO (15%)	$\pi_{aromatic} \rightarrow \pi^*$
			α -HOMO-4 → *α* -LUMO (21%)	$p_{Cl} \rightarrow \pi^*$
			β- HOMO-4 → *β*- LUMO (22%)	$p_{Cl} \rightarrow \pi^*$

	430.44	0.17	α -HOMO-6 → α -LUMO (18%) α -HOMO-4 → α -LUMO (23%) β- HOMO-4 → β-LUMO (28%)	$\pi_{aromatic}$→ π^* p_{Cl} → π^* p_{Cl} → π^*
	415.45	0.09	α -HOMO-8 → α –LUMO (23%) β- HOMO-6 → β- LUMO (63%)	p_{Cl} → π^* $\pi_{aromatic}$→ π^*
2				
648 (0.16), 501 (0.26)[sh], 466 (0.61)[sh], 437 (0.77), 414 (0.68)[sh], 302 (1.6)	646.09	0.03	HOMO-2 → LUMO(30%) HOMO-1 → LUMO(46%)	d_{Ru} → d_{Ru}+ π^* p_{Cl} + d_{Ru} → d_{Ru}+ π^*
	492.13	0.44	HOMO-3→LUMO(80%)	d_{Ru}+ π^*→ d_{Ru}+ π^*
	421.14	0.09	HOMO-6 → LUMO(31%) HOMO-4 → LUMO(62%)	p_{Cl} → d_{Ru}+ π^* $\pi_{aromatic}$→ d_{Ru}+ π^*
3^{Me+}				
744 (0.03)[sh], 578 (0.14), 400 (0.81), 284 (0.87)[sh]	754.24	0.02	HOMO → LUMO (90%)	d_{Ru} → π^*
	547.71	0.05	HOMO-2 → LUMO (49%) HOMO-4 → LUMO (55%)	p_{Cl} + d_{Ru} → π^* $\pi_{aromatic}$→ $\pi_{aromatic}^*$
	447.99	0.26	HOMO-3 → LUMO (81%)	p_{Cl} + π + $\pi_{aromatic}$→ π^*
	394.10	0.25	HOMO-4 → LUMO (86%)	$\pi_{aromatic}$→ π^*
	369.18	0.08	HOMO-7 → LUMO (92%)	p_{Cl} + d_{Ru} → π^*

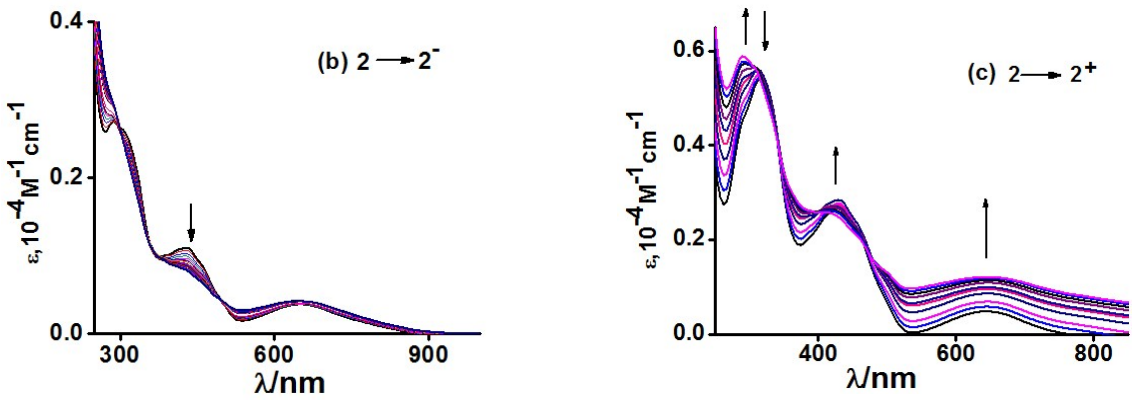

Fig. S9 Spectroelectrochemical measurements showing the change of electronic spectra during the conversions of (a) **2** → **2**$^-$ and (b) **2** → **2**$^+$ in CH_2Cl_2 at 298 K.

Table S5 Gas phase optimized coordinates of gmma (singlet spin state))

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-3.28574	-2.89044	0.160805	19	C	5.232515	-2.10489	1.867403
2	C	-1.91839	-3.08865	0.39555	20	C	7.031968	-0.09662	1.152122
3	C	-1.0061	-2.05665	0.049782	21	C	6.593244	-2.2802	2.111532
4	C	-1.48629	-0.88217	-0.55447	22	H	4.522468	-2.86432	2.180409
5	C	-2.84702	-0.70686	-0.79859	23	C	7.491674	-1.27543	1.745158
6	C	-3.74545	-1.71163	-0.43222	24	H	7.750934	0.66795	0.883613
7	H	-4.0047	-3.65502	0.429313	25	H	6.94662	-3.18664	2.593231
8	H	-0.77625	-0.12273	-0.86748	26	H	8.554872	-1.3981	1.930302
9	H	-3.2004	0.199586	-1.28028	27	S	4.973758	1.562098	0.17236

10	H	-4.80865	-1.58896	-0.61736	28	S	-1.22752	-4.54917	1.14054
11	N	0.353524	-2.30405	0.274566	29	C	-2.69164	-5.61272	1.368033
12	C	1.163068	-1.35181	0.57364	30	H	-2.30561	-6.53845	1.801107
13	H	0.852775	-0.31192	0.73319	31	H	-3.4126	-5.17568	2.063797
14	C	2.583165	-1.63525	0.739255	32	H	-3.17782	-5.84687	0.417302
15	H	2.893456	-2.67515	0.57971	33	C	6.43789	2.625637	-0.05515
16	N	3.392707	-0.68301	1.038339	34	H	7.15884	2.188586	-0.75091
17	C	4.75233	-0.93042	1.263136	35	H	6.05186	3.551362	-0.48823
18	C	5.664628	0.101579	0.917367	36	H	6.924074	2.859792	0.895577

Table S6 Gas phase optimized coordinates of gmma$^-$ (doublet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-3.32335	-2.93727	0.116911	19	C	5.268166	-2.10822	1.754791
2	C	-1.975	-3.10444	0.429742	20	C	7.06958	-0.0498	1.196003
3	C	-1.02419	-2.0631	0.166013	21	C	6.618922	-2.26206	2.063322
4	C	-1.52193	-0.87885	-0.44187	22	H	4.572191	-2.90219	2.005392
5	C	-2.87269	-0.72501	-0.75041	23	C	7.530852	-1.23959	1.784957
6	C	-3.78462	-1.74748	-0.47204	24	H	7.784731	0.73927	0.988746
7	H	-4.0385	-3.72634	0.324167	25	H	6.95898	-3.18264	2.53354
8	H	-0.82596	-0.08488	-0.69247	26	H	8.584993	-1.35132	2.025094
9	H	-3.21275	0.195574	-1.22062	27	S	5.029761	1.585824	0.130058
10	H	-4.83876	-1.63574	-0.71218	28	S	-1.28353	-4.57289	1.182853
11	N	0.278749	-2.3248	0.493704	29	C	-2.76065	-5.63384	1.363082
12	C	1.194388	-1.35688	0.536983	30	H	-2.40027	-6.55883	1.821927
13	H	0.932581	-0.29901	0.418463	31	H	-3.51449	-5.18867	2.020541
14	C	2.551845	-1.63019	0.775931	32	H	-3.21725	-5.87771	0.398321
15	H	2.813652	-2.68806	0.894451	33	C	6.506888	2.646774	-0.05017
16	N	3.467484	-0.66227	0.81921	34	H	7.260722	2.201597	-0.70763
17	C	4.770427	-0.92397	1.146901	35	H	6.14651	3.571762	-0.50902
18	C	5.721234	0.117376	0.883171	36	H	6.963485	2.890643	0.914588

Table S7 Gas phase optimized coordinates of [Zn(gmma)Cl_2] (singlet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	S	9.410724	9.785793	2.091699	21	C	11.01071	17.37925	2.037386
2	C	10.94796	9.02235	2.546555	22	H	11.08149	17.90434	1.089609
3	C	11.22411	7.664599	2.3331	23	C	10.80985	16.00953	4.461588
4	H	10.49439	7.042464	1.824414	24	H	10.66675	15.46579	5.39089

5	C	13.10063	9.234567	3.682015	25	C	11.21821	15.32004	3.305158
6	H	13.85628	9.859077	4.149474	26	N	11.47134	13.93651	3.311214
7	C	11.89871	9.817234	3.231054	27	C	10.61321	18.05745	3.19223
8	N	11.64582	11.19041	3.357144	28	H	10.36967	19.11508	3.141733
9	C	12.42026	7.102817	2.774411	29	C	10.5121	17.36871	4.405095
10	H	12.62081	6.050877	2.589997	30	H	10.17728	17.88348	5.301404
11	C	13.3615	7.889303	3.453309	31	C	11.93883	13.33405	4.349977
12	H	14.30279	7.457226	3.780846	32	H	12.25229	13.87598	5.246766
13	C	12.09011	11.88055	4.350754	33	C	13.54454	14.90146	0.763608
14	H	12.58198	11.4219	5.213208	34	H	13.7705	14.36861	1.690074
15	C	9.135668	9.15086	0.396987	35	H	13.84732	14.27524	-0.0791
16	H	10.00793	9.369983	-0.2232	36	H	14.07285	15.8579	0.733079
17	H	8.273507	9.707854	0.020187	37	Zn	10.74562	12.5332	1.619104
18	H	8.900927	8.083581	0.3944	38	Cl	8.58595	13.28875	1.568422
19	S	11.73713	15.15474	0.565402	39	Cl	12.12012	11.56259	0.041523
20	C	11.3158	16.01473	2.076153					

Table S8 Gas phase optimized coordinates of **1** (triplet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	Ni	11.06566	12.1623	2.393895	21	H	11.16672	8.530291	-0.37806
2	S	10.24429	10.02999	1.314051	22	S	10.244	14.29599	1.317128
3	Cl	13.13899	12.16328	1.181118	23	C	10.98807	15.39093	2.538601
4	Cl	8.961179	12.16129	3.565066	24	C	10.82567	16.77355	2.385757
5	C	10.98882	8.933418	2.533766	25	H	10.24694	17.14969	1.547214
6	C	10.82684	7.550976	2.378824	26	C	12.25672	15.81183	4.574095
7	H	10.24816	7.175933	1.539757	27	H	12.82325	15.45054	5.426295
8	C	12.25777	8.509792	4.568522	28	C	11.69729	14.89569	3.660747
9	H	12.82426	8.869966	5.421215	29	N	11.80903	13.50742	3.801247
10	C	11.69798	9.427153	3.656615	30	C	11.38542	17.66687	3.297588
11	N	11.80933	10.81524	3.799225	31	H	11.25228	18.73613	3.158728
12	C	11.38694	6.656441	3.289246	32	C	12.10879	17.1811	4.393792
13	H	11.25413	5.587352	3.148761	33	H	12.55153	17.87009	5.10753
14	C	12.11025	7.140762	4.386138	34	C	12.29469	12.88907	4.824894
15	H	12.55326	6.450814	5.098784	35	H	12.67516	13.39833	5.711807
16	C	12.29487	11.43216	4.823793	36	C	11.25103	14.73047	-0.15769
17	H	12.67551	10.92167	5.70992	37	H	12.28684	14.42387	-0.00372
18	C	11.2512	9.597983	-0.16158	38	H	10.82354	14.16125	-0.98799
19	H	12.28685	9.905021	-0.00745	39	H	11.16596	15.79839	-0.37285
20	H	10.82314	10.16797	-0.99106					

Table S9 Gas phase optimized coordinates of $\mathbf{1}^{-}$ (doublet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	Ni	11.0657	12.16229	2.371139	21	H	11.22353	8.424352	-0.36146
2	S	10.2483	9.954284	1.27462	22	S	10.24752	14.37176	1.27811
3	Cl	13.10315	12.16384	0.985999	23	C	10.96749	15.43424	2.543598
4	Cl	8.855444	12.16109	3.407494	24	C	10.77054	16.8143	2.449411
5	C	10.96825	8.890084	2.538671	25	H	10.1768	17.20333	1.62548
6	C	10.77149	7.510141	2.442472	26	C	12.23522	15.79658	4.583443
7	H	10.17785	7.122231	1.617943	27	H	12.80812	15.41891	5.424345
8	C	12.23591	8.524961	4.578066	28	C	11.69736	14.88152	3.639154
9	H	12.8087	8.901502	5.41955	29	N	11.82767	13.51796	3.725204
10	C	11.69796	9.441314	3.635079	30	C	11.31212	17.6944	3.390693
11	N	11.82804	10.80477	3.723132	31	H	11.15118	18.76557	3.29783
12	C	11.31315	6.628753	3.382503	32	C	12.05071	17.16836	4.45868
13	H	11.15237	5.55769	3.288073	33	H	12.4806	17.83389	5.205134
14	C	12.05161	7.153344	4.451289	34	C	12.4127	12.86357	4.728917
15	H	12.48156	6.486785	5.196792	35	H	12.87176	13.38029	5.572461
16	C	12.41288	11.45779	4.727851	36	C	11.29664	14.8308	-0.15902
17	H	12.87205	10.9399	5.570618	37	H	12.32732	14.51824	0.017962
18	C	11.29798	9.497731	-0.16289	38	H	10.90051	14.27558	-1.01517
19	H	12.3285	9.810388	0.014854	39	H	11.22176	15.90445	-0.35598
20	H	10.90193	10.05409	-1.01834					

Table S10 Gas phase optimized coordinates of $\mathbf{1}^{2-}$ (singlet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	Ni	13.13717	14.15899	0.05425	21	H	10.00233	8.785051	0.808745
2	S	9.141071	9.735363	2.897807	22	S	11.01947	14.95377	0.29874
3	Cl	15.43683	13.97051	-0.04932	23	C	10.92505	14.79345	2.073235
4	Cl	12.99105	14.83173	-2.1882	24	C	9.891775	15.35737	2.823762
5	C	10.51956	9.070204	3.825569	25	H	9.13257	15.95609	2.320746
6	C	10.26527	7.951147	4.621719	26	C	11.80666	13.72179	4.050131
7	H	9.276913	7.496873	4.5652	27	H	12.51957	13.05992	4.525948
8	C	12.78533	9.119155	4.714944	28	C	11.93377	13.96163	2.642381
9	H	13.76034	9.58985	4.8046	29	N	12.9537	13.50248	1.867475
10	C	11.82125	9.712766	3.821246	30	C	9.823697	15.1471	4.202864
11	N	12.04054	10.78953	3.041098	31	H	9.01871	15.57767	4.79473
12	C	11.23441	7.404694	5.478813	32	C	10.79901	14.31415	4.792026
13	H	11.00835	6.535379	6.094004	33	H	10.75013	14.10746	5.861208
14	C	12.49886	8.015791	5.50959	34	C	13.72119	12.39705	2.236733
15	H	13.2721	7.630088	6.177218	35	H	14.77032	12.48589	1.976007
16	C	13.31124	11.19976	2.784183	36	C	11.31738	16.75768	0.089855
17	H	14.1452	10.50833	2.980086	37	H	12.1429	17.07322	0.731728
18	C	9.767861	9.791277	1.174385	38	H	11.58377	16.89959	-0.95978

19	H	10.65483	10.42708	1.142814	39	H	10.40497	17.30723	0.343475
20	H	8.967227	10.224	0.563713					

Table S11 Gas phase optimized coordinates of **2** (singlet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-0.14665	-1.54378	-1.6475	21	N	1.070514	-2.04562	-1.14425
2	C	-0.8174	-0.43519	-1.09709	22	N	3.352418	-3.13342	-0.57213
3	C	-2.00564	0.026399	-1.65465	23	Cl	3.084712	-2.19839	-3.63035
4	C	-2.54578	-0.60098	-2.78255	24	Cl	0.883691	-5.18723	-0.46113
5	C	-1.88903	-1.69793	-3.34098	25	C	5.554321	-3.49073	0.515807
6	H	-0.41284	0.072906	-0.22853	26	C	-0.70811	-2.18459	-2.77377
7	H	-2.50607	0.883978	-1.21368	27	S	0.12382	-3.60127	-3.53296
8	H	-3.4647	-0.23283	-3.22983	28	S	3.65735	-5.27532	-2.65575
9	H	-2.29056	-2.17633	-4.23001	29	C	-1.11333	-4.91797	-3.19564
10	C	1.740653	-1.50989	-0.1321	30	H	-0.70364	-5.83627	-3.6249
11	C	2.985943	-2.10385	0.180385	31	H	-1.24869	-5.04835	-2.12169
12	C	6.760969	-4.18142	0.568036	32	H	-2.05139	-4.66972	-3.69807
13	C	7.033249	-5.19584	-0.35635	33	Ru	1.999448	-3.61582	-1.96479
14	C	6.084228	-5.51543	-1.32772	34	H	5.367738	-2.70306	1.237445
15	C	4.859115	-4.84454	-1.3735	35	H	7.494063	-3.92148	1.326541
16	C	4.585378	-3.80646	-0.45554	36	C	3.230194	-6.98535	-2.13375
17	H	7.980553	-5.72668	-0.32723	37	H	4.125821	-7.61018	-2.1712
18	H	6.298402	-6.28639	-2.06267	38	H	2.779023	-6.97845	-1.14117
19	H	1.382174	-0.6449	0.416692	39	H	2.501923	-7.35155	-2.86242
20	H	3.607937	-1.70696	0.976474					

Table S12 Gas phase optimized coordinates of **2**$^{-}$ (doublet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-0.13936	-1.54985	-1.65003	21	N	1.048614	-2.04728	-1.16672
2	C	-0.82709	-0.43481	-1.10233	22	N	3.372733	-3.15467	-0.58457
3	C	-2.01257	0.029623	-1.66171	23	Cl	3.115793	-2.14769	-3.65584
4	C	-2.56334	-0.5856	-2.79431	24	Cl	0.869307	-5.19004	-0.4176
5	C	-1.89992	-1.68412	-3.35164	25	C	5.563351	-3.49771	0.513591
6	H	-0.42153	0.069521	-0.23133	26	C	-0.72402	-2.17686	-2.78704
7	H	-2.50912	0.888862	-1.21437	27	S	0.114783	-3.59263	-3.54443
8	H	-3.48155	-0.21242	-3.24086	28	S	3.672257	-5.27978	-2.65958
9	H	-2.29841	-2.16316	-4.24354	29	C	-1.11273	-4.91566	-3.18735
10	C	1.747195	-1.5281	-0.12364	30	H	-0.7194	-5.83077	-3.6407
11	C	2.966259	-2.10911	0.181859	31	H	-1.20346	-5.05949	-2.10945
12	C	6.771336	-4.18493	0.563209	32	H	-2.07242	-4.66281	-3.64743
13	C	7.059628	-5.20085	-0.35852	33	Ru	2.003936	-3.62657	-2.00235
14	C	6.104702	-5.51682	-1.33098	34	H	5.373055	-2.7108	1.235973

15	C	4.878811	-4.85412	-1.37776	35	H	7.501614	-3.91945	1.325567
16	C	4.578564	-3.80532	-0.46207	36	C	3.226227	-6.98197	-2.12158
17	H	8.009922	-5.72793	-0.32826	37	H	4.120312	-7.61199	-2.10696
18	H	6.317271	-6.28689	-2.06957	38	H	2.736187	-6.94665	-1.14713
19	H	1.376879	-0.67991	0.445626	39	H	2.521281	-7.36479	-2.86599
20	H	3.574738	-1.72737	0.997315					

Table S13 Gas phase optimized coordinates of $\mathbf{2}^{+}$ (doublet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-0.15617	-1.52259	-1.65184	21	N	1.068152	-2.00019	-1.14267
2	C	-0.82807	-0.41056	-1.10946	22	N	3.385215	-3.1051	-0.56164
3	C	-2.0252	0.027877	-1.66314	23	Cl	3.080712	-2.14585	-3.52766
4	C	-2.56713	-0.62586	-2.77589	24	Cl	0.951178	-5.06144	-0.46896
5	C	-1.90699	-1.72435	-3.33012	25	C	5.578642	-3.48785	0.517525
6	H	-0.41903	0.11787	-0.25525	26	C	-0.71617	-2.18892	-2.76882
7	H	-2.53164	0.886742	-1.23387	27	S	0.116613	-3.60139	-3.54134
8	H	-3.4939	-0.27463	-3.21922	28	S	3.668087	-5.27624	-2.66678
9	H	-2.31625	-2.21334	-4.20925	29	C	-1.07305	-4.95582	-3.1905
10	C	1.741702	-1.48934	-0.13347	30	H	-0.61527	-5.86956	-3.57719
11	C	2.999613	-2.08988	0.182595	31	H	-1.24742	-5.05019	-2.11904
12	C	6.77086	-4.19988	0.574162	32	H	-1.9985	-4.7563	-3.7346
13	C	7.020148	-5.2286	-0.34187	33	Ru	2.021633	-3.57221	-1.97336
14	C	6.068611	-5.54401	-1.31371	34	H	5.409171	-2.68733	1.229212
15	C	4.857271	-4.85202	-1.36652	35	H	7.511149	-3.94706	1.326803
16	C	4.60549	-3.80141	-0.4506	36	C	3.187516	-6.98026	-2.17737
17	H	7.95734	-5.77573	-0.30815	37	H	4.067139	-7.62375	-2.24416
18	H	6.276933	-6.32451	-2.03952	38	H	2.756663	-6.98882	-1.17642
19	H	1.385511	-0.6353	0.434997	39	H	2.445046	-7.30747	-2.9096
20	H	3.604236	-1.69565	0.994167					

Table S14 Gas phase optimized coordinates of $\mathbf{3}^{\mathbf{Me+}}$ (singlet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-0.14494	-1.50281	-1.64903	27	S	3.691578	-5.25876	-2.6477
2	C	-0.81722	-0.40484	-1.0815	28	C	-1.00826	-4.96052	-3.1975
3	C	-2.05695	-0.00529	-1.57107	29	H	-0.53517	-5.84246	-3.63624
4	C	-2.64297	-0.68492	-2.64481	30	H	-1.11928	-5.09612	-2.12218
5	C	-1.97674	-1.76238	-3.23134	31	H	-1.96356	-4.7742	-3.6925
6	H	-0.37124	0.148516	-0.26176	32	Ru	2.090582	-3.49063	-2.09282
7	H	-2.56268	0.843481	-1.12075	33	H	5.421947	-2.61478	1.190691
8	H	-3.60656	-0.36919	-3.03317	34	H	7.475096	-3.94409	1.398849
9	H	-2.41929	-2.27518	-4.08053	35	C	3.138604	-6.94305	-2.1635
10	C	1.687991	-1.57572	-0.07299	36	H	4.003485	-7.60959	-2.15901

11	C	2.943129	-2.17562	0.242007	37	H	2.637911	-6.90879	-1.19633
12	C	6.744658	-4.20422	0.638749	38	H	2.436642	-7.26351	-2.93762
13	C	6.982081	-5.27734	-0.22755	39	P	3.148255	-2.16389	-3.78325
14	C	6.04747	-5.59246	-1.21542	40	C	4.903628	-1.69632	-3.4574
15	C	4.864397	-4.85757	-1.32849	41	H	5.523441	-2.59149	-3.351
16	C	4.61669	-3.77632	-0.45351	42	H	5.297137	-1.09286	-4.28297
17	H	7.896563	-5.85681	-0.14419	43	H	4.973312	-1.11579	-2.53233
18	H	6.242945	-6.40916	-1.90436	44	C	2.360609	-0.53054	-4.12681
19	H	1.235057	-0.85428	0.600377	45	H	1.323815	-0.66779	-4.44797
20	H	3.462949	-1.91982	1.160416	46	H	2.363167	0.086524	-3.22306
21	N	1.111739	-1.96339	-1.19502	47	H	2.905984	-0.00169	-4.91641
22	N	3.409266	-3.06046	-0.6189	48	C	3.230592	-2.94168	-5.45369
23	Cl	0.976454	-4.97562	-0.47106	49	H	3.721329	-2.26889	-6.16576
24	C	5.577341	-3.45586	0.523395	50	H	3.794673	-3.87766	-5.40288
25	C	-0.73912	-2.18134	-2.73616	51	H	2.221261	-3.1634	-5.81303
26	S	0.122362	-3.55421	-3.54368					

Table S15 Gas phase optimized coordinates of **3^{Me}** (doublet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-0.13735	-1.51786	-1.67968	27	S	3.680353	-5.29053	-2.65847
2	C	-0.84848	-0.4415	-1.09556	28	C	-1.00424	-4.98526	-3.16723
3	C	-2.10084	-0.06667	-1.56986	29	H	-0.56322	-5.86489	-3.64417
4	C	-2.69005	-0.7396	-2.64815	30	H	-1.03964	-5.13159	-2.08704
5	C	-2.00309	-1.8009	-3.24243	31	H	-1.99209	-4.79317	-3.59285
6	H	-0.41456	0.102615	-0.26319	32	Ru	2.092534	-3.51218	-2.14235
7	H	-2.62121	0.762806	-1.09746	33	H	5.41723	-2.67541	1.192923
8	H	-3.66419	-0.43983	-3.02351	34	H	7.445629	-4.03199	1.417566
9	H	-2.44155	-2.32448	-4.08853	35	C	3.09803	-6.95191	-2.13129
10	C	1.801495	-1.45128	-0.21254	36	H	3.952738	-7.62926	-2.0639
11	C	3.027462	-2.03858	0.096199	37	H	2.561481	-6.86688	-1.18546
12	C	6.727011	-4.27504	0.638792	38	H	2.417421	-7.29796	-2.91439
13	C	6.970859	-5.34793	-0.22866	39	P	3.141546	-2.15996	-3.73911
14	C	6.036591	-5.64067	-1.22501	40	C	4.891037	-1.66831	-3.3909
15	C	4.865362	-4.89063	-1.34766	41	H	5.521999	-2.55846	-3.30609
16	C	4.612706	-3.78858	-0.48645	42	H	5.283541	-1.02704	-4.18896
17	H	7.875457	-5.9418	-0.13526	43	H	4.937519	-1.12813	-2.44043
18	H	6.218978	-6.46116	-1.91471	44	C	2.35541	-0.51692	-4.0659
19	H	1.401221	-0.65605	0.409973	45	H	1.328936	-0.65589	-4.41939
20	H	3.592479	-1.70549	0.962356	46	H	2.317763	0.061681	-3.13796
21	N	1.121066	-1.93018	-1.27676	47	H	2.919437	0.046423	-4.81873
22	N	3.459241	-3.05052	-0.68783	48	C	3.276143	-2.86461	-5.44549
23	Cl	0.964691	-4.95288	-0.41019	49	H	3.776039	-2.16501	-6.12599
24	C	5.575677	-3.50548	0.512597	50	H	3.844502	-3.7995	-5.41198

25	C	-0.75546	-2.20208	-2.76095	51	H	2.275486	-3.08542	-5.83058
26	S	0.111063	-3.57885	-3.56017					

Table S16 Gas phase optimized coordinates of $\mathbf{3}^{Me-}$ (singlet spin state)

Sl.	Sym.	X	Y	Z	Sl.	Sym.	X	Y	Z
1	C	-0.12924	-1.54126	-1.70083	27	S	3.677354	-5.33479	-2.66057
2	C	-0.86091	-0.45298	-1.12293	28	C	-1.03996	-5.00436	-3.12742
3	C	-2.09586	-0.06077	-1.62134	29	H	-0.62263	-5.89863	-3.6011
4	C	-2.68753	-0.7089	-2.71971	30	H	-1.04256	-5.13377	-2.04359
5	C	-1.99935	-1.78269	-3.29895	31	H	-2.0398	-4.80716	-3.52458
6	H	-0.44287	0.071719	-0.26938	32	Ru	2.07727	-3.55178	-2.15821
7	H	-2.61253	0.772255	-1.14546	33	H	5.411825	-2.71833	1.19377
8	H	-3.65081	-0.39054	-3.10967	34	H	7.465206	-4.02965	1.37344
9	H	-2.42915	-2.30365	-4.15353	35	C	3.090044	-6.98266	-2.09399
10	C	1.850594	-1.41342	-0.27935	36	H	3.942913	-7.6615	-2.00433
11	C	3.054074	-1.98984	0.023735	37	H	2.551784	-6.86731	-1.15132
12	C	6.747631	-4.27786	0.591906	38	H	2.405168	-7.3494	-2.86548
13	C	7.019001	-5.34002	-0.28848	39	P	3.115815	-2.1792	-3.67624
14	C	6.069587	-5.63625	-1.27473	40	C	4.86043	-1.67493	-3.30055
15	C	4.881756	-4.915	-1.37692	41	H	5.496667	-2.56186	-3.21713
16	C	4.598854	-3.80132	-0.51319	42	H	5.258392	-1.01296	-4.08062
17	H	7.936638	-5.91701	-0.20872	43	H	4.879744	-1.158	-2.33639
18	H	6.252607	-6.44986	-1.97533	44	C	2.333333	-0.52601	-3.98377
19	H	1.48514	-0.56397	0.292785	45	H	1.310598	-0.65913	-4.35113
20	H	3.659851	-1.60518	0.840902	46	H	2.279475	0.022192	-3.03861
21	N	1.098292	-1.94591	-1.31337	47	H	2.909496	0.057083	-4.71396
22	N	3.473856	-3.08419	-0.71487	48	C	3.293489	-2.8181	-5.41234
23	Cl	0.927768	-5.01794	-0.36906	49	H	3.796481	-2.09062	-6.06284
24	C	5.583948	-3.52764	0.491034	50	H	3.871208	-3.74833	-5.39756
25	C	-0.77198	-2.21147	-2.79769	51	H	2.300714	-3.03932	-5.81858
26	S	0.078347	-3.6126	-3.56656					