Supporting Information

DFT/TDDFT study on spectroscopic properties of zinc(II), nickel(II), and palladium(II) metal complexes with thiourea derivative

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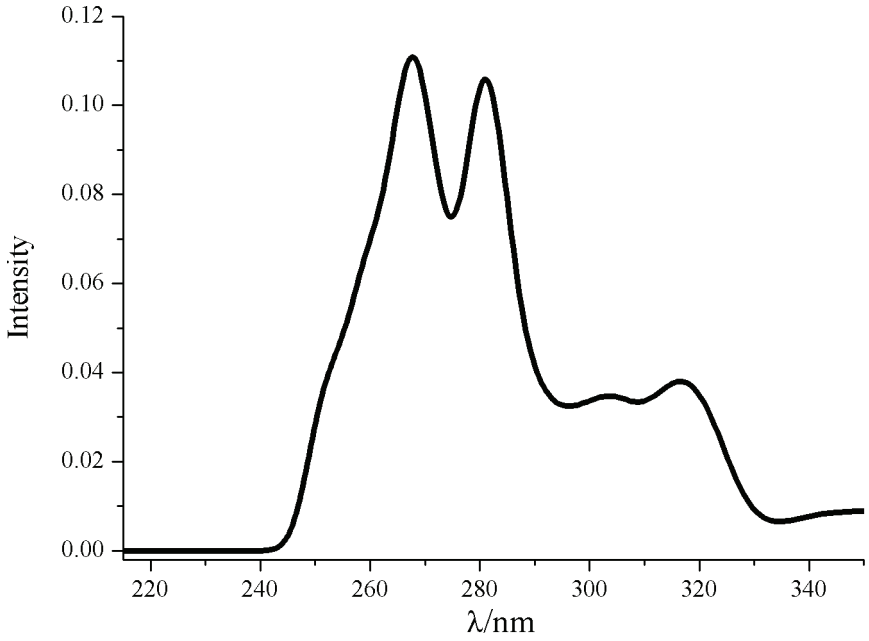

Fig. S1 Simulated absorption spectrum for complex $Ni(C_{10}H_{12}N_3OS)_2$ (**2**) at TDDFT/SAOP level.

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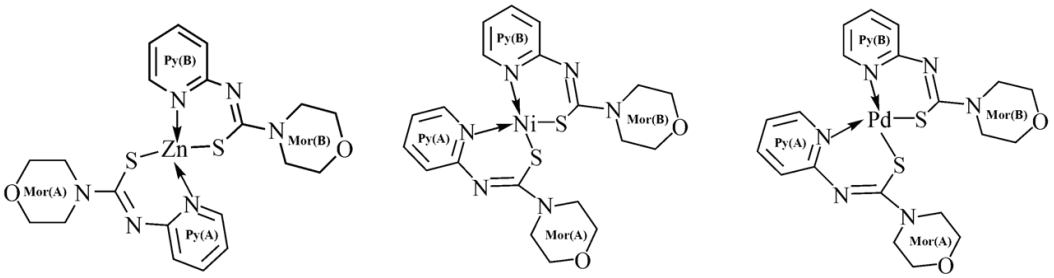

$Zn(C_{10}H_{12}N_3OS)_2$ (**1**) $Ni(C_{10}H_{12}N_3OS)_2$ (**2**) $Pd(C_{10}H_{12}N_3OS)_2$ (**3**)

Fig. S2 Schematic structures of $Zn(C_{10}H_{12}N_3OS)_2$ (**1**), $Ni(C_{10}H_{12}N_3OS)_2$ (**2**), and $Pd(C_{10}H_{12}N_3OS)_2$ (**3**) along with labeling the key atoms and rings.

Table SI Mean unsigned error (MUE) for three different functionals.

Fucntionals	MUE[a]	MUE[b]
B3LYP	0.0389	3.43
B3PW91	0.0269	3.36
M06	0.0286	2.71

[a]based on bondlengths

[b]based on bond angles and dihedral angles

Table SII Cartesian coordinations of the ground state structures for complexes $Zn(C_{10}H_{12}N_3OS)_2$ (**1**), $Ni(C_{10}H_{12}N_3OS)_2$ (**2**), and $Pd(C_{10}H_{12}N_3OS)_2$ (**3**).

$Zn(C_{10}H_{12}N_3OS)_2$				$Ni(C_{10}H_{12}N_3OS)_2$			
N	0.21963	0.20154	1.06073	N	1.22351	-1.62221	-0.68765
C	0.69851	1.43719	0.82563	C	0.57175	-2.67843	-1.22351
C	0.79327	-0.57353	2.01341	C	2.5797	-1.56582	-0.7573
C	1.75298	1.99006	1.5198	C	1.21097	-3.74313	-1.81823
H	0.19428	1.99318	0.03196	H	-0.51461	-2.64868	-1.14512
C	1.87609	-0.05987	2.76499	C	3.28626	-2.65263	-1.32639
C	2.34622	1.21172	2.52385	C	2.61207	-3.72737	-1.85693
H	2.10211	2.99319	1.28652	H	0.63188	-4.56709	-2.22668
H	2.31822	- 0.70426	3.52124	H	4.37133	-2.5863	-1.34028
H	3.17885	1.60446	3.10602	H	3.16277	-4.55269	-2.30617
C	-0.73037	-2.43959	2.17479	C	2.90392	0.7097	-0.26352
S	-2.31772	-1.65135	2.03072	S	1.37324	1.32348	-0.88683
N	-0.77706	-1.72189	-1.39653	N	-0.89521	-1.46301	1.12176
C	-0.74025	-3.06291	-1.28815	C	-0.13498	-2.22015	1.94416
C	-0.44735	-1.13146	-2.5713	C	-2.24981	-1.54608	1.19564
C	-0.39587	-3.90164	-2.32612	C	-0.65686	-3.11734	2.84891
H	-1.00315	-3.46211	-0.30591	H	0.94179	-2.0898	1.84045
C	-0.09094	-1.93922	-3.67661	C	-2.83551	-2.47986	2.08406
C	-0.07187	-3.31076	-3.55565	C	-2.05075	-3.25351	2.90667
H	-0.37934	-4.97948	-2.18267	H	0.00653	-3.70271	3.48006
H	0.17083	-1.4387	-4.6059	H	-3.921	-2.53913	2.09685
H	0.2011	-3.92944	-4.40956	H	-2.50988	-3.95901	3.59782
C	-1.0688	1.1728	-2.20562	C	-2.82735	0.41368	0.03258
S	-2.58998	1.01953	-1.29772	S	-1.39017	1.36294	0.40892
N	-0.34214	0.21458	-2.71664	N	-3.08591	-0.81291	0.42421
N	0.44472	-1.86984	2.21857	N	3.31053	-0.53906	-0.26396
N	-0.73642	-3.80005	2.31019	N	3.78713	1.63502	0.2032
O	-0.57825	-6.68337	2.29565	O	5.68218	3.48632	1.35078
C	0.28051	-5.87302	3.07497	C	6.06257	2.42946	0.49051
H	-0.13823	-5.7484	4.08945	H	6.09533	2.78935	-0.55336
H	1.22706	-6.41826	3.1726	H	7.08145	2.13785	0.77374
C	0.53129	-4.51421	2.46058	C	5.14106	1.23293	0.58122
H	1.19806	-3.92367	3.09977	H	5.47519	0.44006	-0.09737
H	1.03074	-4.60875	1.4801	H	5.14731	0.80731	1.59823
C	-1.92576	-4.64319	2.25539	C	3.46496	3.04121	0.42729
H	-2.70446	-4.13127	1.67808	H	2.39684	3.1328	0.65699
H	-2.33414	-4.8112	3.26573	H	3.65615	3.63917	-0.47922
C	-1.57315	-5.96048	1.59679	C	4.28866	3.55963	1.58713
H	-1.23265	-5.77185	0.56114	H	4.03305	2.9909	2.49864
H	-2.4617	-6.60186	1.54166	H	4.05044	4.61401	1.77335

N	-0.62977	2.44482	-2.44737	N	-3.80358	1.04155	-0.67937
O	0.57548	5.04945	-2.76607	O	-5.87995	2.21711	-2.30486
C	-1.26177	3.66	-1.94509	C	-3.64322	2.33836	-1.33049
H	-1.829	3.42278	-1.03751	H	-2.58901	2.47858	-1.59695
H	-1.98232	4.05897	-2.67818	H	-3.91922	3.15937	-0.6481
C	-0.19251	4.68657	-1.63499	C	-4.50035	2.37589	-2.57805
H	0.47604	4.29146	-0.84695	H	-4.16367	1.58846	-3.27536
H	-0.65423	5.60379	-1.24838	H	-4.38311	3.34228	-3.08351
C	0.6266	4.0538	-3.76981	C	-6.15039	1.43893	-1.15464
H	-0.21314	4.18706	-4.47488	H	-6.24386	2.09572	-0.27138
H	1.55633	4.21578	-4.32848	H	-7.12307	0.95796	-1.31568
C	0.60071	2.64863	-3.21166	C	-5.09439	0.38814	-0.89045
H	0.63968	1.91431	-4.02478	H	-5.3463	-0.19113	0.00496
H	1.47986	2.4609	-2.57012	H	-5.03251	-0.32702	-1.72724
Z	-1.5417	-0.50214	0.14244	Ni	0.08532	-0.22479	0.00881

$Pd(C_{10}H_{12}N_3OS)_2$				
Pd	0.13187	-0.25401	-0.38755	
N	1.44671	-1.77816	-1.04095	
C	0.85747	-2.91488	-1.47053	
C	2.7848	-1.60808	-1.20936	
C	1.54544	-3.95327	-2.05915	
H	-0.21871	-2.97212	-1.31305	
C	3.54088	-2.65584	-1.79087	
C	2.93035	-3.81171	-2.21815	
H	1.01622	-4.84716	-2.37856	
H	4.61154	-2.49711	-1.89449	
H	3.51965	-4.60522	-2.67557	
C	3.0318	0.71904	-0.8087	
S	1.49507	1.30248	-1.46198	
N	-1.04072	-1.54479	0.81149	
C	-0.35198	-2.37651	1.62252	
C	-2.39192	-1.45501	0.92968	
C	-0.94672	-3.18224	2.56862	
H	0.72743	-2.38352	1.47737	
C	-3.05339	-2.27865	1.87397	
C	-2.34156	-3.12683	2.68959	
H	-0.33923	-3.83675	3.18807	
H	-4.13616	-2.19753	1.93121	
H	-2.85944	-3.74588	3.42084	
C	-2.85631	0.51928	-0.30468	
S	-1.39604	1.45044	0.05479	
N	-3.16698	-0.67078	0.14555	

N	3.46505	-0.51682	-0.78865
N	3.89741	1.67128	-0.36108
O	5.7485	3.55957	0.80011
C	6.15611	2.50719	-0.05343
H	6.19434	2.86642	-1.09734
H	7.1769	2.23356	0.24089
C	5.25521	1.29498	0.02945
H	5.60975	0.50875	-0.64701
H	5.2594	0.86708	1.0456
C	3.54631	3.07134	-0.13768
H	2.47566	3.14193	0.08602
H	3.73167	3.67362	-1.04258
C	4.35237	3.60362	1.02812
H	4.10294	3.02759	1.93679
H	4.09212	4.65265	1.21523
N	-3.80182	1.14714	-1.05848
O	-5.80558	2.27727	-2.80442
C	-3.58426	2.38999	-1.79425
H	-2.52154	2.47567	-2.04842
H	-3.8441	3.2651	-1.1757
C	-4.41633	2.36842	-3.0589
H	-4.09523	1.52232	-3.69194
H	-4.25574	3.29201	-3.62844
C	-6.1249	1.58459	-1.61261
H	-6.21736	2.30145	-0.77725
H	-7.10859	1.12324	-1.76435
C	-5.10909	0.52248	-1.25481
H	-5.39817	0.01459	-0.32748
H	-5.0527	-0.25154	-2.03799

Table SIII Molecular orbital compositions in the ground state for $Zn(C_{10}H_{12}N_3OS)_2$ (**1**) at M06/6-31+G(d)-LANL2DZ level in dimethylformamide.

MO	Energy	Contribution											Assignment
	(eV)	Py(A)	Py(B)	Mor(A)	Mor(B)	S(1)	S(2)	C(1)	C(3)	N(2)	N(4)	Zn	
L+2	-0.93	37	37	0	0	0	0	0	0	0	0	0	π^*[Py(A)+Py(B)]
L+1	-1.23	14	14	0	0	0	0	0	0	0	0	0	π^*[Py(A)+Py(B)]
L	-1.39	12	12	0	0	0	0	0	0	0	0	0	π^*[Py(A)+Py(B)]
H	-6.37	0	0	0	0	0	0	0	0	13	13	0	p[N(2)+N(4)]
H-1	-6.37	0	0	0	0	0	10	0	0	13	14	0	p[S(2)+N(2)+N(4)]
H-2	-6.78	0	0	0	0	31	31	0	0	0	0	0	p[S(1)+S(2)]
H-3	-6.80	0	0	0	0	29	29	0	0	0	0	0	p[S(1)+S(2)]

Table SIV Molecular orbital compositions in the ground state for $Ni(C_{10}H_{12}N_3OS)_2$ (**2**) at M06/6-31+G(d)-LANL2DZ level in dimethylformamide.

MO	Energy	Contribution											Assignment
	(eV)	Py(A)	Py(B)	Mor(A)	Mor(B)	S(1)	S(2)	C(1)	C(2)	N(2)	N(4)	Ni	
L+2	-1.28	14	14	0	0	0	0	0	0	0	0	0	π^*[Py(A)+Py(B)]
L+1	-1.33	22	22	0	0	0	0	0	0	0	0	0	π^*[Py(A)+Py(B)]
L	-2.10	0	0	0	0	15	15	0	0	0	0	46	p[S(1)+S(2)]+d(Ni)
H	-6.23	0	0	0	0	11	11	0	0	11	11	13	p[S(1)+S(2)+N(2)+N(4)]+d(Ni)
H-1	-6.31	0	0	0	0	17	17	0	0	11	11	0	p[S(1)+S(2)+N(2)+N(4)]
H-2	-6.53	0	0	13	13	13	13	0	0	0	0	12	p[S(1)+S(2)+Mor(A)+Mor(B)]+d(Ni)
H-3	-6.64	0	0	0	0	23	23	0	0	0	0	12	p[S(1)+S(2)]+d(Ni)

Table SV Molecular orbital compositions in the ground state for $Pd(C_{10}H_{12}N_3OS)_2$ (**3**) at M06/6-31+G(d)-LANL2DZ level in dimethylformamide.

MO	Energy	Contribution										Assignment
	(eV)	Py(A)	Py(B)	Mor(A)	Mor(B)	S(1)	S(2)	C(1)	C(2)	N(2)	N(4)	Pd	
L+2	-1.25	14	14	0	0	0	0	0	0	0	0	0	π^*[Py(A)+Py(B)]
L+1	-1.31	13	13	0	0	0	0	0	0	0	0	0	π^*[Py(A)+Py(B)]
L	-2.31	0	0	0	0	17	17	0	0	0	0	39	p[S(1)+S(2)]+d(Pd)
H	-6.15	0	0	0	0	17	17	0	0	0	0	17	p[S(1)+S(2)]+d(Pd)
H-1	-6.34	0	0	0	0	14	14	0	0	12	12	0	p[S(1)+S(2)+N(2)+N(4)]
H-2	-6.56	0	0	12	12	17	17	0	0	0	0	14	p[S(1)+S(2)+Mor(A)+Mor(B)]+d(Pd)
H-3	-6.64	0	0	0	0	15	15	0	0	0	0	0	p[S(1)+S(2)]