Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 81 (11) S347–S350 (2016) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

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

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J. Serb. Chem. Soc. 81 (11) (2016) 1263–1272

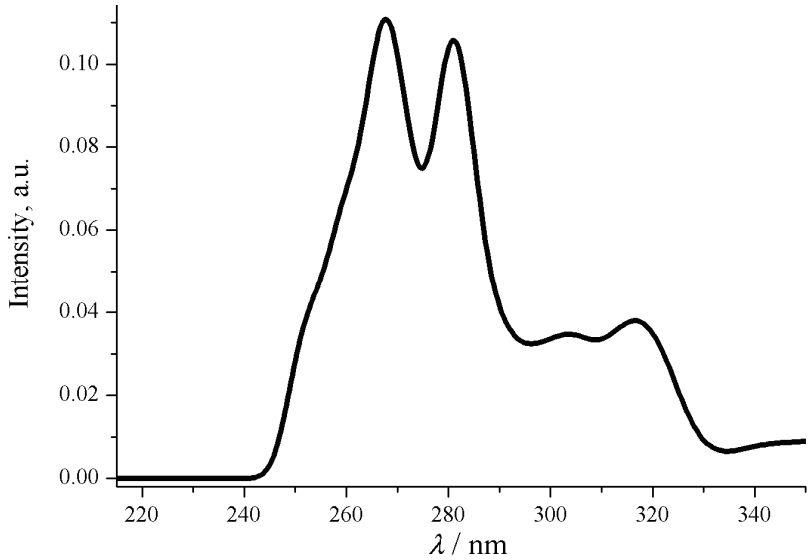

Fig. S-1. Simulated absorption spectrum for complex $Ni(C_{10}H_{12}N_3OS)_2$ (**2**) at the TD-DFT/SAOP level.

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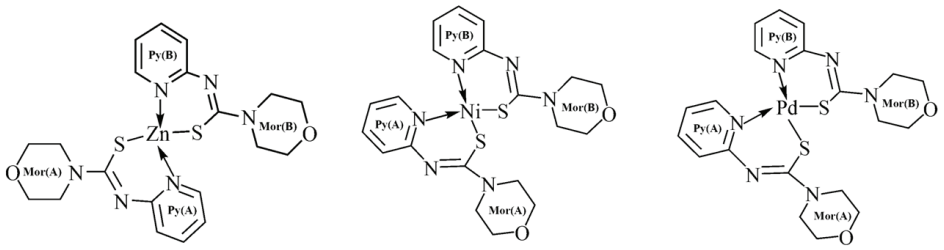

$Zn(C_{10}H_{12}N_3OS)_2$ (**1**) $Ni(C_{10}H_{12}N_3OS)_2$ (**2**) $Pd(C_{10}H_{12}N_3OS)_2$ (**3**)

Fig. S-2. 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 the labeling of the key atoms and rings.

TABLE S-I. Mean unsigned error (*MUE*) for the three different functionals

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

[a]Based on bond lengths; [b]based on bond angles and dihedral angles

TABLE S-II. Cartesian coordinates 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**)

$Zn(C_{10}H_{12}N_3OS)_2$				$Ni(C_{10}H_{12}N_3OS)_2$				$Pd(C_{10}H_{12}N_3OS)_2$			
N	0.21963	0.20154	1.06073	N	1.22351	–1.62221	–0.68765	Pd	0.13187	–0.25401	–0.38755
C	0.69851	1.43719	0.82563	C	0.57175	–2.67843	–1.22351	N	1.44671	–1.77816	–1.04095
C	0.79327	–0.57353	2.01341	C	2.5797	–1.56582	–0.7573	C	0.85747	–2.91488	–1.47053
C	1.75298	1.99006	1.5198	C	1.21097	–3.74313	–1.81823	C	2.7848	–1.60808	–1.20936
H	0.19428	1.99318	0.03196	H	–0.51461	–2.64868	–1.14512	C	1.54544	–3.95327	–2.05915
C	1.87609	–0.05987	2.76499	C	3.28626	–2.65263	–1.32639	H	–0.21871	–2.97212	–1.31305
C	2.34622	1.21172	2.52385	C	2.61207	–3.72737	–1.85693	C	3.54088	–2.65584	–1.79087
H	2.10211	2.99319	1.28652	H	0.63188	–4.56709	–2.22668	C	2.93035	–3.81171	–2.21815
H	2.31822	–	0.70426	H	4.37133	–2.5863	–1.34028	H	1.01622	–4.84716	–2.37856
H	3.17885	1.60446	3.10602	H	3.16277	–4.55269	–2.30617	H	4.61154	–2.49711	–1.89449
C	–0.73037	–2.43959	2.17479	C	2.90392	0.7097	–0.26352	H	3.51965	–4.60522	–2.67557
S	–2.31772	–1.65135	2.03072	S	1.37324	1.32348	–0.88683	C	3.0318	0.71904	–0.8087
N	–0.77706	–1.72189	–1.39653	N	–0.89521	–1.46301	1.12176	S	1.49507	1.30248	–1.46198
C	–0.74025	–3.06291	–1.28815	C	–0.13498	–2.22015	1.94416	N	–1.04072	–1.54479	0.81149
C	–0.44735	–1.13146	–2.5713	C	–2.24981	–1.54608	1.19564	C	–0.35198	–2.37651	1.62252
C	–0.39587	–3.90164	–2.32612	C	–0.65686	–3.11734	2.84891	C	–2.39192	–1.45501	0.92968
H	–1.00315	–3.46211	–0.30591	H	0.94179	–2.0898	1.84045	C	–0.94672	–3.18224	2.56862
C	–0.09094	–1.93922	–3.67661	C	–2.83551	–2.47986	2.08406	H	0.72743	–2.38352	1.47737
C	–0.07187	–3.31076	–3.55565	C	–2.05075	–3.25351	2.90667	C	–3.05339	–2.27865	1.87397
H	–0.37934	–4.97948	–2.18267	H	0.00653	–3.70271	3.48006	C	–2.34156	–3.12683	2.68959
H	0.17083	–1.4387	–4.6059	H	–3.921	–2.53913	2.09685	H	–0.33923	–3.83675	3.18807
H	0.2011	–3.92944	–4.40956	H	–2.50988	–3.95901	3.59782	H	–4.13616	–2.19753	1.93121
C	–1.0688	1.1728	–2.20562	C	–2.82735	0.41368	0.03258	H	–2.85944	–3.74588	3.42084
S	–2.58998	1.01953	–1.29772	S	–1.39017	1.36294	0.40892	C	–2.85631	0.51928	–0.30468

TABLE S-II. Continued

$Zn(C_{10}H_{12}N_3OS)_2$				$Ni(C_{10}H_{12}N_3OS)_2$				$Pd(C_{10}H_{12}N_3OS)_2$			
N	–0.34214	0.21458	–2.71664	N	–3.08591	–0.81291	0.42421	S	–1.39604	1.45044	0.05479
N	0.44472	–1.86984	2.21857	N	3.31053	–0.53906	–0.26396	N	–3.16698	–0.67078	0.14555
N	–0.73642	–3.80005	2.31019	N	3.78713	1.63502	0.2032	N	3.46505	–0.51682	–0.78865
O	–0.57825	–6.68337	2.29565	O	5.68218	3.48632	1.35078	N	3.89741	1.67128	–0.36108
C	0.28051	–5.87302	3.07497	C	6.06257	2.42946	0.49051	O	5.7485	3.55957	0.80011
H	–0.13823	–5.7484	4.08945	H	6.09533	2.78935	–0.55336	C	6.15611	2.50719	–0.05343
H	1.22706	–6.41826	3.1726	H	7.08145	2.13785	0.77374	H	6.19434	2.86642	–1.09734
C	0.53129	–4.51421	2.46058	C	5.14106	1.23293	0.58122	H	7.1769	2.23356	0.24089
H	1.19806	–3.92367	3.09977	H	5.47519	0.44006	–0.09737	C	5.25521	1.29498	0.02945
H	1.03074	–4.60875	1.4801	H	5.14731	0.80731	1.59823	H	5.60975	0.50875	–0.64701
C	–1.92576	–4.64319	2.25539	C	3.46496	3.04121	0.42729	H	5.2594	0.86708	1.0456
H	–2.70446	–4.13127	1.67808	H	2.39684	3.1328	0.65699	C	3.54631	3.07134	–0.13768
H	–2.33414	–4.8112	3.26573	H	3.65615	3.63917	–0.47922	H	2.47566	3.14193	0.08602
C	–1.57315	–5.96048	1.59679	C	4.28866	3.55963	1.58713	H	3.73167	3.67362	–1.04258
H	–1.23265	–5.77185	0.56114	H	4.03305	2.9909	2.49864	C	4.35237	3.60362	1.02812
H	–2.4617	–6.60186	1.54166	H	4.05044	4.61401	1.77335	H	4.10294	3.02759	1.93679
N	–0.62977	2.44482	–2.44737	N	–3.80358	1.04155	–0.67937	H	4.09212	4.65265	1.21523
O	0.57548	5.04945	–2.76607	O	–5.87995	2.21711	–2.30486	N	–3.80182	1.14714	–1.05848
C	–1.26177	3.66	–1.94509	C	–3.64322	2.33836	–1.33049	O	–5.80558	2.27727	–2.80442
H	–1.829	3.42278	–1.03751	H	–2.58901	2.47858	–1.59695	C	–3.58426	2.38999	–1.79425
H	–1.98232	4.05897	–2.67818	H	–3.91922	3.15937	–0.6481	H	–2.52154	2.47567	–2.04842
C	–0.19251	4.68657	–1.63499	C	–4.50035	2.37589	–2.57805	H	–3.8441	3.2651	–1.1757
H	0.47604	4.29146	–0.84695	H	–4.16367	1.58846	–3.27536	C	–4.41633	2.36842	–3.0589
H	–0.65423	5.60379	–1.24838	H	–4.38311	3.34228	–3.08351	H	–4.09523	1.52232	–3.69194
C	0.6266	4.0538	–3.76981	C	–6.15039	1.43893	–1.15464	H	–4.25574	3.29201	–3.62844
H	–0.21314	4.18706	–4.47488	H	–6.24386	2.09572	–0.27138	C	–6.1249	1.58459	–1.61261
H	1.55633	4.21578	–4.32848	H	–7.12307	0.95796	–1.31568	H	–6.21736	2.30145	–0.77725
C	0.60071	2.64863	–3.21166	C	–5.09439	0.38814	–0.89045	H	–7.10859	1.12324	–1.76435
H	0.63968	1.91431	–4.02478	H	–5.3463	–0.19113	0.00496	C	–5.10909	0.52248	–1.25481
H	1.47986	2.4609	–2.57012	H	–5.03251	–0.32702	–1.72724	H	–5.39817	0.01459	–0.32748
Zn	–1.5417	–0.50214	0.14244	Ni	0.08532	–0.22479	0.00881	H	–5.0527	–0.25154	–2.03799

TABLE S-III. Compositions of the molecular orbitals in the ground state for $Zn(C_{10}H_{12}N_3OS)_2$ (**1**) in dimethylformamide at the M06/6-31+G(d)-LANL2DZ level

MO	Energy eV	Contribution											Assignment
		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 S-IV. Compositions of the molecular orbitals in the ground state for $Ni(C_{10}H_{12}N_3OS)_2$ (**2**) in dimethylformamide at the M06/6-31+G(d)-LANL2DZ level

MO	Energy eV	Contribution											Assignment
		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 S-V. Compositions of the molecular orbitals in the ground state for $Pd(C_{10}H_{12}N_3OS)_2$ (**3**) in dimethylformamide at the M06/6-31+G(d)-LANL2DZ level

MO	Energy eV	Contribution											Assignment
		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)]