Supporting Information

Synthesis, Crystal Structures, Magnetic Properties and Theoretical Investigation of a New Series of Ni^{II}-Ln^{III}-W^{V} Heterotrimetallics: Understanding the SMM Behavior of Mixed Polynuclear Complexes

Veacheslav Vieru[1], Traian D. Pasatoiu[2], Liviu Ungur[1,3], Elizaveta Suturina[1,4], Augustin M. Madalan,[2] Carine Duhayon[5,6], Jean-Pascal Sutter[5,6], Marius Andruh[2*], Liviu F. Chibotaru[1*]

[1]. Theory of Nanomaterials Group, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee (Belgium). e-mail: Liviu.Chibotaru@chem.kuleuven.be

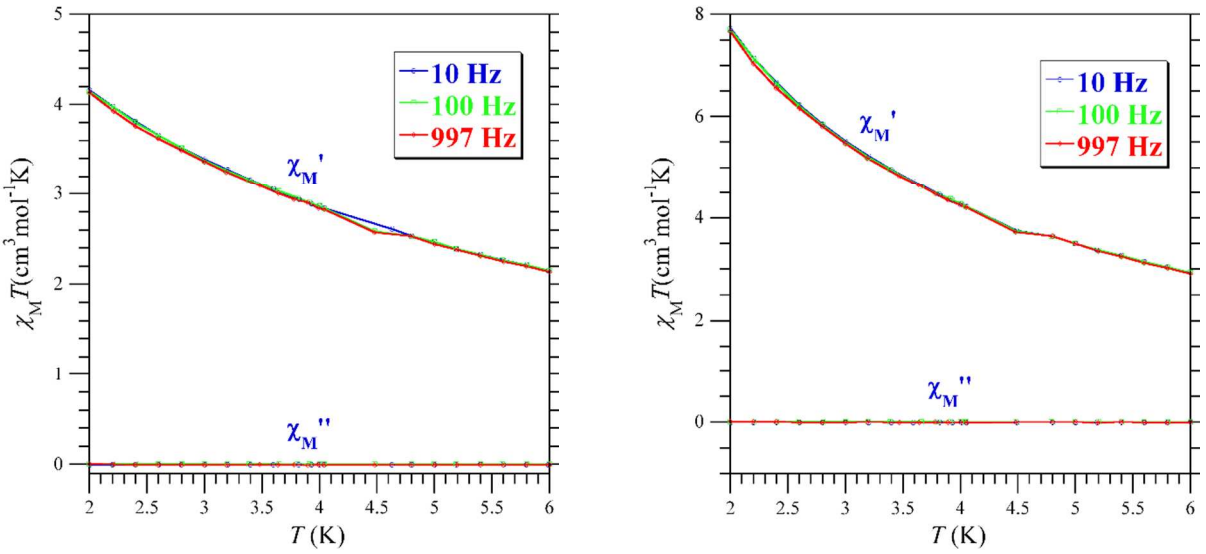
[2]. Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str.Dumbrava Rosie 23, 020464 Bucharest (Romania). e-mail: marius.andruh@dnt.ro

[3]. Theoretical Chemistry, Lund University, Getingevagen 60, 22241, Lund, Sweden

[4]. Novosibirsk State University, Pirogova 2, 630090, Novosibirsk, Russia

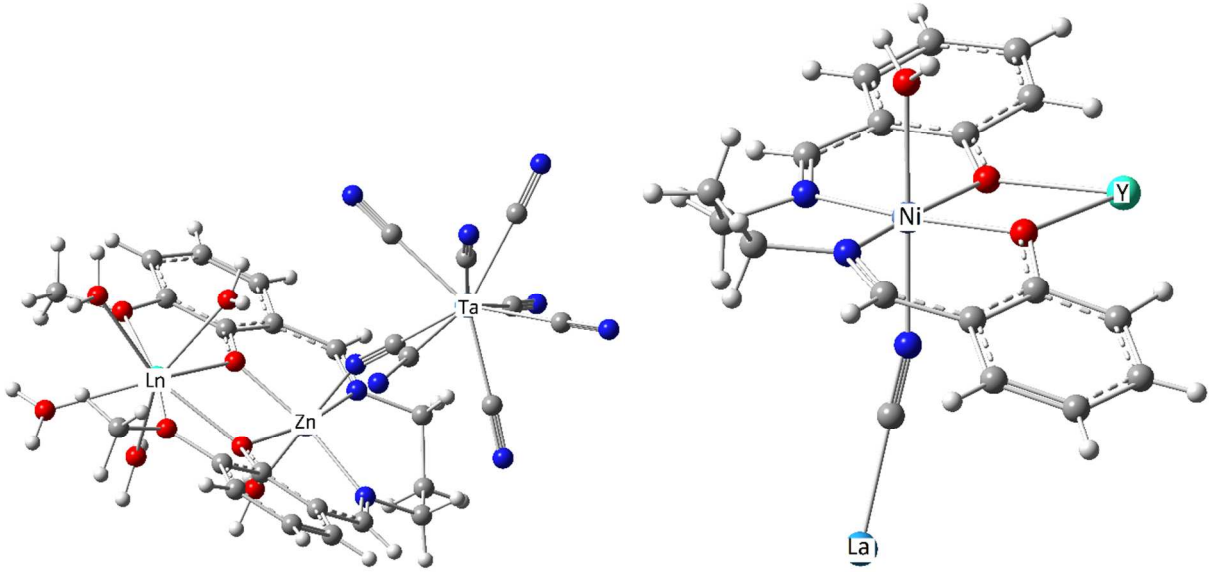
[5]. CNRS, LCC (Laboratoire de Chimie de Coordination), 205, route de Narbonne, F-31077 Toulouse, France

[6]. Université de Toulouse; UPS, INPT ; LCC ; F-31077 Toulouse, France



(a) (b)

Figure S1. The temperature dependence of the in-phase (top), and out-of-phase (bottom) signals for **4** (a) and **5** (b), at different frequencies of the oscillating field.



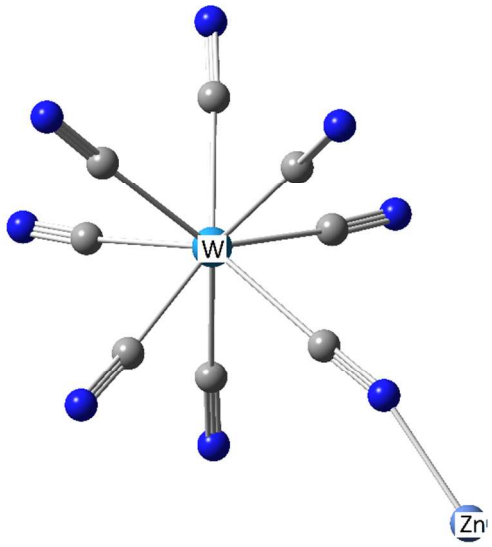


Figure S2. Structure of the fragments used in *ab initio* calculations.

Table S1: Contractions of the employed basis set.

Basis set	Definition	Contraction
1	Ln[a]: ANO-RCC-VDZ	7s6p4d2f
	Ni, Zn: ANO-RCC-VDZ	5s4p2d
	W, Ta: ANO-RCC-VDZ	7s6p4d2f
	Y: ANO-RCC-VDZ	6s5p3d
	O, N: ANO-RCC-VDZ	3s2p
	C: ANO-DK3	2s1p
	H: ANO-DK3	1s
	La: ECP.deGraaf.0s.0s.0e-La (LaMnO3).	0
	Zn: ECP.Lopez-Moraza.0s.0s.0e-AIMP-KZnF3.	0
	Y: ECP.Abdalla.0s.0s.0e-AIMP-Cs2NaYCl6.	0
2	Ln, W: ANO-RCC- VTZP	8s7p5d3f2g1h
	Ni: ANO-RCC-VTZP	6s5p3d2f1g
	Ta: ANO-RCC-VDZ	7s6p4d2f
	Y: ANO-RCC-VDZ	6s5p3d
	Zn: ANO-RCC-VDZ	5s4p2d
	C, N, O[b]: ANO-RCC-VTZ	4s3p2d
	C, N: ANO-RCC-VDZ	3s2p
	H: ANO-RCC-VDZ	2s

[a] Ln=Dy, Gd, Tb or Y

[b] Only C, N and O direct coordinated to the metal

Table S2. A comparison of the W-fragment CASSCF energies (cm^{-1}) obtained within different basis sets.

1		3		4		5	
Basis set 1	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**
0	0	0	0	0	0	0	0
33165	32320	33583	32893	32925	32184	33098	32390
37847	37248	37725	36868	37594	36856	37759	37146
42506	42059	42621	42250	42627	42325	41787	41437
47237	47792	47008	47461	46326	46899	47015	47599

Table S3. Spin-orbit energies (cm^{-1}) of W-fragment.

1		3		4		5	
Basis set 1	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
32269	31657	32585	32093	32020	31488	32148	31652
32269	31657	32585	32093	32020	31488	32148	31652
38503	37791	38507	37571	38315	37476	38443	37741
38503	37791	38507	37571	38315	37476	38443	37741
42911	42385	42972	42529	42880	42546	42245	41803
42911	42385	42972	42529	42880	42546	42245	41803
47980	48355	47781	48044	47179	47536	47747	48166
47980	48355	47781	48044	47179	47536	47747	48166

Table S4. *g*-factors of the ground KD of W ions obtained within different basis sets.

1		3		4		5	
Basis set 1	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**
1.95	1.96	1.96	1.97	1.96	1.97	1.95	1.96
1.88	1.91	1.90	1.91	1.89	1.91	1.88	1.90
1.77	1.82	1.79	1.83	1.78	1.82	1.76	1.81

Table S5. A comparison of the Ni-fragment CASPT2 energies (cm^{-1}) obtained within different basis sets.

1		3		4		5	
Basis set 1	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**
0	0	0	0	0	0	0	0
8378	7787	8487	7972	8322	7782	8363	7838
8683	8132	8852	8359	8668	8165	8758	8262
12820	12937	13008	13130	12612	12726	13012	13149
15156	13886	15263	14043	15033	13779	15094	13857
17921	17811	18082	17982	17653	17532	18036	17906
18218	18158	18434	18379	18006	17951	18316	18238
27724	26048	28107	26310	27798	25946	27873	26135
29470	28194	29688	28410	29239	27961	29618	28335
30664	29474	30966	29746	30565	29379	30865	29671
…	…	…	…	…	…	…	…

Table S6. A comparison of the Ln-fragment CASSCF energies (cm^{-1}) obtained within different basis sets.

3		4		5	
Basis set 1	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**
0	0	0	0	0	0
40819	40889	53	31	8	3
40822	40890	129	108	128	98
40851	40913	330	334	150	108
43576	43644	497	476	247	209
43582	43652	588	515	277	240
43588	43654	816	744	342	302
43591	43658	25603	25678	472	383
43598	43664	25618	25684	493	404
43601	43666	25697	25764	636	561
43608	43672	25769	25808	654	580
43612	43682	25787	25829	7569	7558
43617	43683	29141	29195	7651	7640
43638	43711	29145	29199	7702	7677
…	…	…	…	…	…

Table S7. A comparison of the Ln-fragment spin-orbit energies (cm^{-1}) obtained within different basis sets.

3		4		5	
Basis set 1	**Basis set 2**	**Basis set 1**	**Basis set 2**	**Basis set 1**	**Basis set 2**
0	0	0	0	0	0
0	0	0.58	1.09	0	0
0.43	0.40	88	75	132	118
0.43	0.40	93	83	132	118
0.79	0.65	187	160	187	174
0.79	0.65	205	194	187	174
1.36	0.88	250	229	236	214
1.36	0.88	310	261	236	214
39534	39604	324	272	293	239
39534	39604	361	386	293	239
39588	39655	369	389	344	272
39588	39655	564	459	344	272
39626	39691	565	460	476	383
39626	39691	2212	2183	476	383
39673	39711	2216	2183	596	532
39673	39711	2268	2230	596	532
40045	40117	2284	2242	3636	3596
40045	40117	2330	2295	3636	3596
40084	40156	2347	2315	3691	3649
40084	40156	2364	2324	3691	3649
40138	40188	2431	2363	3774	3728
40138	40188	2443	2380	3774	3728
40584	40649	2540	2481	3839	3784
40584	40649	2550	2492	3839	3784
40637	40693	3578	3533	3917	3832
40637	40693	3615	3567	3917	3832
42992	43057	3637	3577	3968	3852
42992	43057	3680	3622	3968	3852
43013	43075	3734	3680	4029	3929
43013	43075	3774	3722	4029	3929
…	…	…	…	…	…

Table S8. Low-lying CASPT2/SO-RASSI energies (cm^{-1}) of Ni-fragment.

Basis set 2					
7	**8a**	**8b**	**9**	**10**	**11**
0	0	0	0	0	0
8	7	9	9	9	9
13	12	11	14	13	11
8427	8439	8398	7978	8207	8524
8535	8546	8528	8077	8313	8655
8726	8730	8770	8273	8507	8891
9290	9376	9030	8922	9120	9158
9360	9430	9152	8990	9187	9275
9462	9536	9280	9093	9293	9403
…	…	…	…	…	…

Table S9. Low-lying CASSCF/SO-RASSI energies (cm^{-1}) of W-fragment.

Basis set 2					
7	**8a**	**8b**	**9**	**10**	**11**
0	0	0	0	0	0
0	0	0	0	0	0
32266	32205	32208	31950	31894	32672
32266	32205	32208	31950	31894	32672
36715	37408	36726	37161	37147	36955
36715	37408	36726	37161	37147	36955
43458	44089	43757	44794	43655	44012
43458	44089	43757	44794	43655	44012
47696	47314	47654	48207	47420	48177
47696	47314	47654	48207	47420	48177

Table S10. CASSCF/RASSI spin-orbit energies (cm^{-1}) and the *g*-factors in the ground doublet of the Ln fragments.

7 **(Gd)***	**8a** **(Tb)**	**8b** **(Tb)**	**9** **(Dy)***	**10** **(Ho)**	**11** **(Er)***
0	0	0	0	0	0
0.11	0.13	0.013	65.6	6.39	35.9
0.23	112	199	111	19.2	66.2
0.43	113	200	158	35.2	88.6
	142	289	208	60.2	141
	152	294	223	66.6	182
	181	316	280	72.7	220
	203	329	408	86.0	259
	218	343		120	
	263	380		133	
	266	396		148	
	343	421		162	
	344	428		170	
				185	
				191	
				233	
				234	
g-factors of the ground doublet states**					
1.99	0	0	0.070	0	0.49
1.99	0	0	0.16	0	1.32
1.99	17.8	17.9	18.7	15.5	15.3

* Twofold degenerate energy levels corresponding to Kramers doublets.

** The g-factor is given for S=7/2 of Gd and for $\tilde{s}$ =1/2 of Tb, Dy, Ho and Er fragments, respectively.