Supporting Information File

to

Exploring High-Symmetry Lanthanide-Functionalized Polyoxopalladates as Building Blocks for Quantum Computing

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1. Computational Details (DFT)

Density functional theory (DFT) calculations were performed using the Amsterdam Density Functional program (ADF2017).[1] Numerical integration was performed using the Becke grid integration.[2] The computational screening of **1-Na** was performed within the local density approximation (LDA, VWN density functional)[3a] and the GGA Becke exchange plus the Perdew 86 correlation (BP) functional.[3b,3c] We used all-electron Slater basis sets of triple-zeta quality with one or two polarization functions (TZP and TZ2P, resp.).[4] Scalar relativistic effects were accounted for using the Zeroth-Order Regular Approximation (ZORA).[5] Solvation effects were introduced using the COnductor-like Screening MOdel (COSMO) with the default parameters for water (ε = 78.39; solvent radius = 1.93 Å).[6] The spin-unrestricted (= U) formalism was used for the high-spin open-shell electronic system **1-Gd**. Next to geometry optimizations at BP86/TZ2P/ZORA-Scalar/COSMO, single-point calculations using the hybrid B3LYP functional[7] were performed to calculate different molecular properties (bonding energies, frontier molecular orbitals, and molecular electrostatic potentials) of the five models **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu**.

2. Choice of theoretical level for geometry calculations

Geometry optimization of polyanion **1-Na** using LDA and BP functionals and TZP or TZ2P basis sets is summarized in Table S1.

- Calculations at LDA level leads to more accurate estimation of the Se-O and the Pd-O bond lengths, however the dimensions of the inner cavity (Figure S1) and the Ln-O are over estimated.
- Calculations at BP level lead to more accurate estimation of the dimensions of the inner cavity and the Ln-O bond lengths.
- The at both levels, the basis set only induces difference on pm scale (i.e. contraction in case of TZ2P).

Table S1: Characteristic bond lengths of polyanion **1-Na** system as calculated at different theoretical levels. All bond lengths and interatomic distances are compared to the reported crystal structure in reference [8]. Calculated values that are within the experimental ranges are colored green, while those that do not are in red.

Length/ distance	Experiment [Å] Ref. [8]	BP/TZP/ZSC/COSMO Length/distance [Å]	**BP/TZ2P/ZSC/COSMO Length/distance [Å]**	LDA/TZP/ZSC/COSMO Length/distance [Å]	LDA/TZ2P/ZSC/COSMO Length/distance [Å]
Se-O	1.655-1.718	1.745; 1.746	**1.731**	1.718	1.705; 1.713
Pd-O	1.960-2.038	2.009	**1.998**	1.961	1.953
Pd-O_{Se}	1.997-2.062	2.094	**2.072**	2.033	2.045
Na···O	**2.642-2.786**	2.650	**2.644**	2.568	2.574
d_1(O···O)	**2.699-2.811**	2.707	**2.701**	2.631	2.643
d_2(O···O)	**2.666-2.803**	2.678	**2.672**	2.592	2.596

3. Comparison to the Preyssler System

The structure of the Preyssler type polyoxoanions $[P_5W_{30}O_{110}]^{15-}$ (Figure S1) exhibits an ideal D_{5h}. This polyanion exhibits two pentagonal entrances $\{W_5O_5\}$ fragments which are comparable to the entrance site of the $\{Pd_5O_5\}$ fragment polyanion **1** (see Figure S1). The entrance is wide enough to allow permeation of a variety of cations (alkali, earth alkali, lanthanides, actinides etc.).[9] However, it must be stressed that in the case of lanthanides, the inner cavity is not suitable for encapsulation due to its dimensions. Thus, the incorporated lanthanides are incorporated between the pentagonal entrance and the pentagonal face of the cavity prism. The lanthanide centers adopt pentagonal antiprism or capped pentagonal antiprism coordination geometry when in the latter case they additionally bind to an outer water molecule.[9]

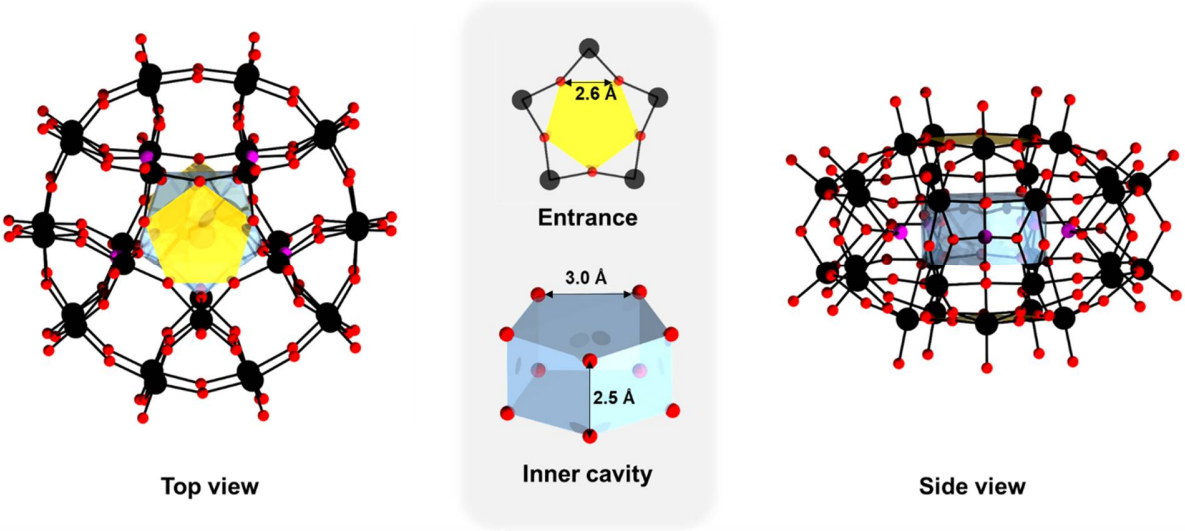

Figure S1: Combined ball-and-stick and polyhedral representation of the $[P_5W_{30}O_{110}]^{15-}$ polyanion shown in top (left) and side view (right). Color code: W = black, P = purple, O = red spheres. The inner cavity defined by the $\{O_{10}\}$ pentagonal prism is shown in blue prism, while the pentagonal entrance comprised of the five μ_2-O atoms is shown in yellow color.

4. Structural and electronic properties of 1, 1-Na, 1-La, 1-Gd and 1-Lu

The calculated bond distances and interatomic distances for systems **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu** are summarized in Table S2. The calculated Mulliken charge populations of the three inequivalent O centers (Figure S2) are summarized in Table S3. Spin density isosurface of polyanion **1-Gd** is depicted in Figures S3. The HOMO-LUMO gap energies and distribution of the frontier orbitals over different atoms are presented in Tables S4 and S5.

Table S2: Characteristic bond lengths and interatomic distances in polyanions **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu** as calculated at BP/TZ2P/ZSC/COSMO-water levels.

Bond/distance	Length/distance [Å]				
Polyanion	**1**	**1-Na**	**1-La**	**1-Gd**	**1-Lu**
Se-O	1.731	1.731	1.732; 1.733	1.731; 1.732	1.731; 1.732
Pd-O	1.994	1.998	2.008	2.001	1.999
Pd-O_{Se}	2.092	2.072	2.064	2.058	2.060
Na···O	-	2.644	2.642	2.592	2.559
d_1(O···O)	2.692	2.701	2.714	2.671	2.646
d_2(O···O)	2.673	2.672	2.665	2.611	2.575

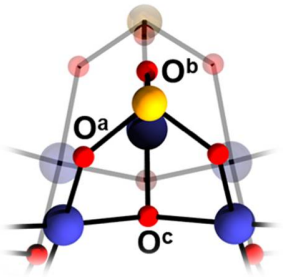

Figure S2. Ball-and-stick representation depicting segment of the **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu** polanions. The segment shows the three topologically inequivalent O atoms in the vicinity of the {SeO_3} groups. Color code: Pd= blue, O = red, and Se = yellow spheres.

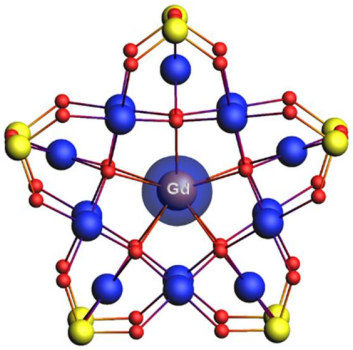

Figure S3: Spin density isosurface of 1-Gd indicating accumulation of α spins at the Gd^{III} center as calculated at UB3LYP/TZ2P/ZSC/COSMO level. Color code: Pd = blue, O = red, and Se = yellow spheres.

Table S3: Mulliken charge populations of **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu** obtained at (U)B3LYP/TZ2P/ZSC/COSMO for different O atoms following the labeling in Figure S2.

Polyanion	**Charge**		
	O_a	**O_b**	**O_c**
1	-0.78	-0.78	-0.79
1-Na	-0.67	-0.67	-0.71
1-La	-0.75	-0.75	-0.96
1-Gd	-0.75	-0.75	-0.97
1-Lu	-0.75	-0.75	-0.95

Table S4: HOMO, LUMO and HOMO-LUMO gap (ΔLUMO-HOMO) energies in eV of **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu,** calculated at (U)B3LYP/TZ2P/ZSC/COSMO.

	Polyanion				
	1	**1-Na**	**1-La**	**1-Gd**	**1-Lu**
HOMO [eV]	-4.1	-4.5	-5.2	-5.2	-5.2
LUMO [eV]	-0.7	-1.0	-1.6	-1.6	-1.6
$\Delta_{LUMO-HOMO}$ [eV]	3.5	3.5	3.6	3.5	3.6

Table S5: Contributions (in %) of the Kohn-Sham orbitals centered on palladium, oxygen, selenium and the incorporated cations to the HOMO and the LUMO orbitals of **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu**.

Polyanion	Distribution [%]			
1	Pd	O	Se	NA
HOMO	41.4	48.5	1.5	-
LUMO	53.6	31.5	6.7	-
$\Delta_{LUMO-HOMO}$	**12.1**	**-17.0**	**5.3**	**-**
1-Na	Pd	O	Se	Na
HOMO	70.2	20.6	0.0	0
LUMO	55.0	30.0	8.1	0
$\Delta_{LUMO-HOMO}$	**-15.3**	**9.5**	**8.1**	**0**
1-La	Pd	O	Se	La
HOMO	70.6	18.7	0.0	0.0
LUMO	55.5	26.8	6.4	3.6
$\Delta_{LUMO-HOMO}$	**-15.2**	**8.1**	**6.4**	**3.6**
1-Gd	Pd	O	Se	Gd
HOMO	70.3	18.8	0.0	0.0
LUMO	55.1	26.4	6.2	5.0
$\Delta_{LUMO-HOMO}$	**-15.2**	**7.6**	**6.2**	**5.0**
1-Lu	Pd	O	Se	Lu
HOMO	69.5%	18.8%	0.0	0.0
LUMO	55.2%	27.1%	6.2	4.4
$\Delta_{LUMO-HOMO}$	**-14.3%**	**8.3%**	**6.2**	**4.4**

5. Ligand Field Analysis

The model that we have applied in order to predict the magnetic states and the ground state wave function is the Radial Effective Charge (REC) model. Such a model is an electrostatic *semi-empirical* crystal field approach commonly used in molecular magnetism, which provides a computationally inexpensive estimation of the crystal field parameters (CFPs) and permit to rationalize the magnetic properties of a particular *f*-block coordination complex.[10] From the calculated CFPs, the model estimates the ground-*J* multiplet energy levels and their corresponding wave functions, composed by the different M_J microstates. This kind of calculations use the atomic coordinates of the first coordination sphere around the magnetic centre as an input. The software code that has this model implemented is the SIMPRE computational package,[11] which parameterizes the electric field effect produced by the surrounding ligands by using the following Crystal Field Hamiltonian expressed in terms of the Extended Stevens Operators (ESOs)[12]:

$$\hat{H}_{cf}(J) = \sum_{k=2,4,6}\sum_{q=-k}^{k} B_k^q O_k^q = \sum_{k=2,4,6}\sum_{q=-k}^{k} a_k(1-\sigma_k)A_k^q \left\langle r^k \right\rangle O_k^q \tag{1}$$

where k is the order (also called rank or degree) and q is the operator range, that varies between k and $-k$, of the Stevens operator equivalents O_k^q as defined by Ryabov in terms of the angular momentum operators $J_\pm$ and J_z, where the components $O_k^q(c)$ and $O_k^q(s)$ correspond to the ESOs with $q \geq 0$ and $q < 0$ respectively.[13] Note that all the Stevens CF parameters B_k^q are real, whereas the matrix elements of O_k^q ($q < O$) are imaginary. a_k are the α, β and γ Stevens coefficients[14] for k = 2, 4, 6, respectively, which are tabulated and depend on the number of *f* electrons. σ_k are the Sternheimer shielding parameters[15] of the 4*f* electronic shell, and $\langle r^k \rangle$ are the expectation values of the radius.

In the code, the A_k^q CF parameters are calculated through the following expressions:

$$A_k^0 = \frac{4\pi}{2k+1}\sum_{i=1}^{N}\frac{Z_i e^2}{R_i^{k+1}} Z_{k0}(\theta_i,\varphi_i) p_{kq} \tag{2.a}$$

$$A_k^q = \frac{4\pi}{2k+1}\sum_{i=1}^{N}\frac{Z_i e^2}{R_i^{k+1}} Z_{kq}^c(\theta_i,\varphi_i) p_{kq} \tag{2.b}$$

$$A_k^q = \frac{4\pi}{2k+1}\sum_{i=1}^{N}\frac{Z_i e^2}{R_i^{k+1}} Z_{k|q|}^s(\theta_i,\varphi_i) p_{k|q|} \tag{2.c}$$

and the effect of the ligand is modeled through an effective point charge situated between the lanthanoid and the coordinated atom at a distance R_i from the magnetic center, which is smaller than the real metal-ligand distance (r_i). To account for the effect of covalent electron sharing, a radial displacement vector (D_r) is defined, in which the polar coordinate r of each coordinated atom is varied, $R_i = r_i - D_r$. The usual procedure is to obtain the D_r parameter of each kind of donor atom fitting an observable (e.g. energy levels or magnetic properties). At the same time, the charge value (Z_i) is scanned in order to achieve the minimum deviation between calculated and experimental data, whereas θ_i and φ_i remain constant. This allows to inexpensively correlate the chemical structure with ligand field effects.

In this work, we have used the REC parameters D_r = 0.8 Å and Z_i = 0.197 determined by Baldoví *et al*. in the study of the $[LnPd_{12}(AsPh)_8O_{32}]^{5-}$ series as a starting point.[16] Due to the different coordination environment between that family of lanthanide-based polyoxopalladates and $[LnPd_{15}Se_{10}O_{40}]^{7-}$, the parameter D_r have been scanned between 0.6 and 1.2 Å (step 0.1 Å) to explore a wider range of possibilities, while keeping fixed the relation $f = D_r \cdot Z_i = 0.1576$. As an illustrative example, the resulting set of CFPs, energy levels and compositions of the wave functions for D_r = 1.0 Å and Z_i = 0.1576 are reported in Tables S6 and S7.

Table S6. Crystal-field parameters ($A_k^q < r^k >$; Stevens notation) in cm^{-1} calculated for **1-Tb**, **1-Dy**, **1-Ho** and **1-Er.**

k	*q*	1-Tb	1-Dy	1-Ho	1-Er
2	0	-274.50	-258.78	-243.24	-227.15
4	0	-120.00	-110.68	-102.74	-95.99
6	0	36.72	32.62	29.19	26.33

Table S7. Ground multiplet energy level scheme (cm^{-1}) and main $|M_J>$ contributions to the wave function calculated for **1-Tb**, **1-Dy**, **1-Ho** and **1-Er .**

1-Tb		1-Dy		1-Ho		1-Er	
0	100% |0>	**0**	|±1/2>	**0**	50% |+4> + 50% |-4>	**0**	|±13/2>
20	50% |+1> + 50% |-1>	**4**	|±11/2>	**26**	50% |+5> + 50% |-5>	**20**	|±15/2>
78	50% |+2> + 50% |-2>	**8**	|±9/2>	**37**	50% |+3> + 50% |-3>	**33**	|±1/2>
171	50% |+3> + 50% |-3>	**10**	|±3/2>	**105**	50% |+2> + 50% |-2>	**82**	|±3/2>
267	65% |+6> + 35% |-6>	**20**	|±5/2>	**119**	50% |+6> + 50% |-6>	**113**	|±11/2>
278	50% |+4> + 50% |-4>	**21**	|±7/2>	**166**	50% |+1> + 50% |-1>	**156**	|±5/2>
345	50% |+5> + 50% |-5>	**77**	|±13/2>	**190**	100% |0>	**199**	|±9/2>
		375	|±15/2>	**200**	50% |+8> + 50% |-8>	**209**	|±7/2>
				225	50% |+7> + 50% |-7>		

6. Coordinates

Cartesian coordinates (in Å) of **1**, **1-Na**, **1-La**, **1-Gd** and **1-Lu** as calculated on (U)BP/TZ2P/ZSC/COSMO level.

1: $[Pd_{15}O_{10}(SeO_3)_{10}]^{10-}$ (D_{5h})			
Se	-5.15109846	-0.00000000	-3.06712817
O	1.83943972	1.33643106	1.34607842
O	1.83943972	1.33643106	-1.34607842
O	1.83943972	-1.33643106	1.34607842
O	1.83943972	-1.33643106	-1.34607842
O	-0.70260321	-2.16239087	1.34607842
O	-0.70260321	-2.16239087	-1.34607842
O	-2.27367215	-0.00000000	1.34607842
O	-2.27367215	-0.00000000	-1.34607842
O	-0.70260321	2.16239087	1.34607842
O	-0.70260321	2.16239087	-1.34607842
Pd	2.93600505	-0.00000000	2.34029563
Pd	3.02529806	2.19800757	0.00000000
Pd	0.90727557	2.79230657	2.34029563
Pd	2.93600505	-0.00000000	-2.34029563
Pd	0.90727557	2.79230657	-2.34029563
Pd	3.02529806	-2.19800757	0.00000000
Pd	0.90727557	-2.79230657	2.34029563
Pd	0.90727557	-2.79230657	-2.34029563
Pd	-2.37527767	-1.72574037	2.34029563
Pd	-1.15556080	-3.55645096	0.00000000
Pd	-2.37527767	-1.72574037	-2.34029563
Pd	-2.37527767	1.72574037	2.34029563
Pd	-3.73947367	-0.00000000	0.00000000
Pd	-2.37527767	1.72574037	-2.34029563
Pd	-1.15556080	3.55645096	0.00000000
O	4.15895319	1.32875260	3.39607708
O	4.15895319	-1.32875260	3.39607708
O	4.33215972	3.14749815	1.34784654
O	4.33215972	3.14749815	-1.34784654
O	0.02146851	4.36600650	3.39607708
O	2.54890616	3.54479223	3.39607708
O	4.15895319	1.32875260	-3.39607708
O	4.15895319	-1.32875260	-3.39607708
O	0.02146851	4.36600650	-3.39607708
O	2.54890616	3.54479223	-3.39607708
O	4.33215972	-3.14749815	-1.34784654
O	4.33215972	-3.14749815	1.34784654
O	0.02146851	-4.36600650	3.39607708
O	2.54890616	-3.54479223	3.39607708
O	0.02146851	-4.36600650	-3.39607708
O	2.54890616	-3.54479223	-3.39607708
O	-2.58364231	-3.51955469	3.39607708
O	-4.14568468	-1.36958781	3.39607708
O	-1.65473753	-5.09275898	1.34784654
O	-1.65473753	-5.09275898	-1.34784654
O	-2.58364231	-3.51955469	-3.39607708
O	-4.14568468	-1.36958781	-3.39607708
O	-4.14568468	1.36958781	3.39607708
O	-2.58364231	3.51955469	3.39607708
O	-5.35484351	-0.00000000	1.34784654
O	-5.35484351	-0.00000000	-1.34784654
O	-4.14568468	1.36958781	-3.39607708
O	-2.58364231	3.51955469	-3.39607708
O	-1.65473753	5.09275898	1.34784654
O	-1.65473753	5.09275898	-1.34784654
Se	4.16732651	3.02773981	3.06712817
Se	4.16732651	-3.02773981	3.06712817
Se	4.16732651	3.02773981	-3.06712817
Se	-1.59177685	4.89898592	3.06712817
Se	4.16732651	-3.02773981	-3.06712817
Se	-1.59177685	4.89898592	-3.06712817
Se	-1.59177685	-4.89898592	3.06712817
Se	-1.59177685	-4.89898592	-3.06712817
Se	-5.15109846	-0.00000000	3.06712817

1-Na: $[NaPd_{15}O_{10}(SeO_3)_{10}]^{9-}$ (D_{5h})			
Na	-0.00000022	-0.00000000	0.00000000
O	1.83907834	1.33616879	1.35062860
O	1.83907834	1.33616879	-1.35062860
O	1.83907834	-1.33616879	1.35062860
O	1.83907834	-1.33616879	-1.35062860
O	-0.70246572	-2.16196652	1.35062860
O	-0.70246572	-2.16196652	-1.35062860
O	-2.27322634	-0.00000000	1.35062860
O	-2.27322634	-0.00000000	-1.35062860
O	-0.70246572	2.16196652	1.35062860
O	-0.70246572	2.16196652	-1.35062860
Pd	2.93954442	-0.00000000	2.34866493
Pd	3.02941268	2.20099731	0.00000000
Pd	0.90836903	2.79567308	2.34866493
Pd	2.93954442	-0.00000000	-2.34866493
Pd	0.90836903	2.79567308	-2.34866493
Pd	3.02941268	-2.20099731	0.00000000
Pd	0.90836903	-2.79567308	2.34866493
Pd	0.90836903	-2.79567308	-2.34866493
Pd	-2.37814179	-1.72782099	2.34866493
Pd	-1.15713298	-3.56128845	0.00000000
Pd	-2.37814179	-1.72782099	-2.34866493
Pd	-2.37814179	1.72782099	2.34866493
Pd	-3.74456049	-0.00000000	0.00000000
Pd	-2.37814179	1.72782099	-2.34866493
Pd	-1.15713298	3.56128845	0.00000000
O	4.15486389	1.32530168	3.39303064
O	4.15486389	-1.32530168	3.39303064
O	4.32569517	3.14280166	1.34206175
O	4.32569517	3.14280166	-1.34206175
O	0.02348660	4.36105132	3.39303064
O	2.54436020	3.54196984	3.39303064
O	4.15486389	1.32530168	-3.39303064
O	4.15486389	-1.32530168	-3.39303064
O	0.02348660	4.36105132	-3.39303064
O	2.54436020	3.54196984	-3.39303064
O	4.32569517	-3.14280166	-1.34206175
O	4.32569517	-3.14280166	1.34206175
O	0.02348660	-4.36105132	3.39303064
O	2.54436020	-3.54196984	3.39303064
O	0.02348660	-4.36105132	-3.39303064
O	2.54436020	-3.54196984	-3.39303064
O	-2.58236310	-3.51435943	3.39303064
O	-4.14034867	-1.36997626	3.39303064
O	-1.65226883	-5.08515991	1.34206175
O	-1.65226883	-5.08515991	-1.34206175
O	-2.58236310	-3.51435943	-3.39303064
O	-4.14034867	-1.36997626	-3.39303064
O	-4.14034867	1.36997626	3.39303064
O	-2.58236310	3.51435943	3.39303064
O	-5.34685376	-0.00000000	1.34206175
O	-5.34685376	-0.00000000	-1.34206175
O	-4.14034867	1.36997626	-3.39303064
O	-2.58236310	3.51435943	-3.39303064
O	-1.65226883	5.08515991	1.34206175
O	-1.65226883	5.08515991	-1.34206175
Se	4.16243300	3.02418476	3.06120924
Se	4.16243300	-3.02418476	3.06120924
Se	4.16243300	3.02418476	-3.06120924
Se	-1.58990823	4.89323372	3.06120924
Se	4.16243300	-3.02418476	-3.06120924
Se	-1.58990823	4.89323372	-3.06120924
Se	-1.58990823	-4.89323372	3.06120924
Se	-1.58990823	-4.89323372	-3.06120924
Se	-5.14505063	-0.00000000	3.06120924
Se	-5.14505063	-0.00000000	-3.06120924

1-La: $[LaPd_{15}O_{10}(SeO_3)_{10}]^{7-}$ (D_{5h})			
La	0.00000099	0.00000000	0.00000000
O	1.83422520	1.33264189	1.35708367
O	1.83422520	1.33264189	-1.35708367
O	1.83422520	-1.33264189	1.35708367
O	1.83422520	-1.33264189	-1.35708367
O	-0.70061031	-2.15625988	1.35708367
O	-0.70061031	-2.15625988	-1.35708367
O	-2.26722481	0.00000000	1.35708367
O	-2.26722481	0.00000000	-1.35708367
O	-0.70061031	2.15625988	1.35708367
O	-0.70061031	2.15625988	-1.35708367
Pd	2.94500870	0.00000000	2.36771485
Pd	3.03766881	2.20699486	0.00000000
Pd	0.91005842	2.80086878	2.36771485
Pd	2.94500870	0.00000000	-2.36771485
Pd	0.91005842	2.80086878	-2.36771485
Pd	3.03766881	-2.20699486	0.00000000
Pd	0.91005842	-2.80086878	2.36771485
Pd	0.91005842	-2.80086878	-2.36771485
Pd	-2.38256030	-1.73103210	2.36771485
Pd	-1.16028487	-3.57099269	0.00000000
Pd	-2.38256030	-1.73103210	-2.36771485
Pd	-2.38256030	1.73103210	2.36771485
Pd	-3.75476293	0.00000000	0.00000000
Pd	-2.38256030	1.73103210	-2.36771485
Pd	-1.16028487	3.57099269	0.00000000
O	4.14572285	1.31697252	3.39047711
O	4.14572285	-1.31697252	3.39047711
O	4.31228607	3.13305850	1.33347614
O	4.31228607	3.13305850	-1.33347614
O	0.02858420	4.34978268	3.39047711
O	2.53361480	3.53584890	3.39047711
O	4.14572285	1.31697252	-3.39047711
O	4.14572285	-1.31697252	-3.39047711
O	0.02858420	4.34978268	-3.39047711
O	2.53361480	3.53584890	-3.39047711
O	4.31228607	-3.13305850	-1.33347614
O	4.31228607	-3.13305850	1.33347614
O	0.02858420	-4.34978268	3.39047711
O	2.53361480	-3.53584890	3.39047711
O	0.02858420	-4.34978268	-3.39047711
O	2.53361480	-3.53584890	-3.39047711
O	-2.57986142	-3.50224732	3.39047711
O	-4.12805547	-1.37134102	3.39047711
O	-1.64714534	-5.06939514	1.33347614
O	-1.64714534	-5.06939514	-1.33347614
O	-2.57986142	-3.50224732	-3.39047711
O	-4.12805547	-1.37134102	-3.39047711
O	-4.12805547	1.37134102	3.39047711
O	-2.57986142	3.50224732	3.39047711
O	-5.33027650	0.00000000	1.33347614
O	-5.33027650	0.00000000	-1.33347614
O	-4.12805547	1.37134102	-3.39047711
O	-2.57986142	3.50224732	-3.39047711
O	-1.64714534	5.06939514	1.33347614
O	-1.64714534	5.06939514	-1.33347614
Se	4.15185527	3.01649871	3.05498473
Se	4.15185527	-3.01649871	3.05498473
Se	4.15185527	3.01649871	-3.05498473
Se	-1.58586623	4.88079743	3.05498473
Se	4.15185527	-3.01649871	-3.05498473
Se	-1.58586623	4.88079743	-3.05498473
Se	-1.58586623	-4.88079743	3.05498473
Se	-1.58586623	-4.88079743	-3.05498473
Se	-5.13197313	0.00000000	3.05498473
Se	-5.13197313	0.00000000	-3.05498473

1: Gd $[GdPd_{15}O_{10}(SeO_3)_{10}]^{7-}$ (D_{5h})			
Gd	-0.00000007	-0.00000000	0.00000000
O	1.79670793	1.30538477	1.33565068
O	1.79670793	1.30538477	-1.33565068
O	1.79670793	-1.30538477	1.33565068
O	1.79670793	-1.30538477	-1.33565068
O	-0.68628146	-2.11215692	1.33565068
O	-0.68628146	-2.11215692	-1.33565068
O	-2.22085329	-0.00000000	1.33565068
O	-2.22085329	-0.00000000	-1.33565068
O	-0.68628146	2.11215692	1.33565068
O	-0.68628146	2.11215692	-1.33565068
Pd	2.92198025	-0.00000000	2.35246027
Pd	3.01050042	2.18725664	0.00000000
Pd	0.90294151	2.77896842	2.35246027
Pd	2.92198025	-0.00000000	-2.35246027
Pd	0.90294151	2.77896842	-2.35246027
Pd	3.01050042	-2.18725664	0.00000000
Pd	0.90294151	-2.77896842	2.35246027
Pd	0.90294151	-2.77896842	-2.35246027
Pd	-2.36393180	-1.71749694	2.35246027
Pd	-1.14990893	-3.53905558	0.00000000
Pd	-2.36393180	-1.71749694	-2.35246027
Pd	-2.36393180	1.71749694	2.35246027
Pd	-3.72118332	-0.00000000	0.00000000
Pd	-2.36393180	1.71749694	-2.35246027
Pd	-1.14990893	3.53905558	0.00000000
O	4.13201501	1.30991421	3.38036484
O	4.13201501	-1.30991421	3.38036484
O	4.29475890	3.12032504	1.32393561
O	4.29475890	3.12032504	-1.32393561
O	0.03106037	4.33456562	3.38036484
O	2.52266526	3.52499412	3.38036484
O	4.13201501	1.30991421	-3.38036484
O	4.13201501	-1.30991421	-3.38036484
O	0.03106037	4.33456562	-3.38036484
O	2.52266526	3.52499412	-3.38036484
O	4.29475890	-3.12032504	-1.32393561
O	4.29475890	-3.12032504	1.32393561
O	0.03106037	-4.33456562	3.38036484
O	2.52266526	-3.52499412	3.38036484
O	0.03106037	-4.33456562	-3.38036484
O	2.52266526	-3.52499412	-3.38036484
O	-2.57292224	-3.48848038	3.38036484
O	-4.11281875	-1.36899467	3.38036484
O	-1.64045202	-5.04879197	1.32393561
O	-1.64045202	-5.04879197	-1.32393561
O	-2.57292224	-3.48848038	-3.38036484
O	-4.11281875	-1.36899467	-3.38036484
O	-4.11281875	1.36899467	3.38036484
O	-2.57292224	3.48848038	3.38036484
O	-5.30861411	-0.00000000	1.32393561
O	-5.30861411	-0.00000000	-1.32393561
O	-4.11281875	1.36899467	-3.38036484
O	-2.57292224	3.48848038	-3.38036484
O	-1.64045202	5.04879197	1.32393561
O	-1.64045202	5.04879197	-1.32393561
Se	4.14140800	3.00890909	3.04494858
Se	4.14140800	-3.00890909	3.04494858
Se	4.14140800	3.00890909	-3.04494858
Se	-1.58187719	4.86851718	3.04494858
Se	4.14140800	-3.00890909	-3.04494858
Se	-1.58187719	4.86851718	-3.04494858
Se	-1.58187719	-4.86851718	3.04494858
Se	-1.58187719	-4.86851718	-3.04494858
Se	-5.11906197	-0.00000000	3.04494858
Se	-5.11906197	-0.00000000	-3.04494858

1-Lu: $[LuPd_{15}O_{10}(SeO_3)_{10}]^{7-}$ (D_{5h})			
Lu	-0.00000007	-0.00000000	0.00000000
O	1.77181341	1.28729785	1.32315721
O	1.77181341	1.28729785	-1.32315721
O	1.77181341	-1.28729785	1.32315721
O	1.77181341	-1.28729785	-1.32315721
O	-0.67677260	-2.08289167	1.32315721
O	-0.67677260	-2.08289167	-1.32315721
O	-2.19008198	-0.00000000	1.32315721
O	-2.19008198	-0.00000000	-1.32315721
O	-0.67677260	2.08289167	1.32315721
O	-0.67677260	2.08289167	-1.32315721
Pd	2.90737343	-0.00000000	2.34496041
Pd	2.99248011	2.17416411	0.00000000
Pd	0.89842775	2.76507651	2.34496041
Pd	2.90737343	-0.00000000	-2.34496041
Pd	0.89842775	2.76507651	-2.34496041
Pd	2.99248011	-2.17416411	0.00000000
Pd	0.89842775	-2.76507651	2.34496041
Pd	0.89842775	-2.76507651	-2.34496041
Pd	-2.35211464	-1.70891126	2.34496041
Pd	-1.14302579	-3.51787143	0.00000000
Pd	-2.35211464	-1.70891126	-2.34496041
Pd	-2.35211464	1.70891126	2.34496041
Pd	-3.69890899	-0.00000000	0.00000000
Pd	-2.35211464	1.70891126	-2.34496041
Pd	-1.14302579	3.51787143	0.00000000
O	4.12321339	1.30506327	3.37494130
O	4.12321339	-1.30506327	3.37494130
O	4.28215247	3.11116593	1.31789213
O	4.28215247	3.11116593	-1.31789213
O	0.03295404	4.32469576	3.37494130
O	2.51533189	3.51812230	3.37494130
O	4.12321339	1.30506327	-3.37494130
O	4.12321339	-1.30506327	-3.37494130
O	0.03295404	4.32469576	-3.37494130
O	2.51533189	3.51812230	-3.37494130
O	4.28215247	-3.11116593	-1.31789213
O	4.28215247	-3.11116593	1.31789213
O	0.03295404	-4.32469576	3.37494130
O	2.51533189	-3.51812230	3.37494130
O	0.03295404	-4.32469576	-3.37494130
O	2.51533189	-3.51812230	-3.37494130
O	-2.56865289	-3.47938242	3.37494130
O	-4.10284677	-1.36774570	3.37494130
O	-1.63563680	-5.03397223	1.31789213
O	-1.63563680	-5.03397223	-1.31789213
O	-2.56865289	-3.47938242	-3.37494130
O	-4.10284677	-1.36774570	-3.37494130
O	-4.10284677	1.36774570	3.37494130
O	-2.56865289	3.47938242	3.37494130
O	-5.29303170	-0.00000000	1.31789213
O	-5.29303170	-0.00000000	-1.31789213
O	-4.10284677	1.36774570	-3.37494130
O	-2.56865289	3.47938242	-3.37494130
O	-1.63563680	5.03397223	1.31789213
O	-1.63563680	5.03397223	-1.31789213
Se	4.13429078	3.00373812	3.03928453
Se	4.13429078	-3.00373812	3.03928453
Se	4.13429078	3.00373812	-3.03928453
Se	-1.57915865	4.86015038	3.03928453
Se	4.13429078	-3.00373812	-3.03928453
Se	-1.57915865	4.86015038	-3.03928453
Se	-1.57915865	-4.86015038	3.03928453
Se	-1.57915865	-4.86015038	-3.03928453
Se	-5.11026459	-0.00000000	3.03928453
Se	-5.11026459	-0.00000000	-3.03928453

7. References

1. a) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.;Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931– 967, DOI: 10.1002/jcc.1056. (b) ADF 2017, SCM, Theoretical Chemistry, Vrije Univesity, Amsterdam, The Netherlands, http://www.scm.com.

2. (a) Becke, A. D. A multicenter numerical integration scheme for polyatomic molecules. *J. Chem. Phys.* **1988**, *88*, 2547– 2553, DOI: 10.1063/1.454033. (b) Franchini, M.; Philipsen, P. H. T.; Visscher, L. The Becke Fuzzy Cells Integration Scheme in the Amsterdam Density Functional Program Suite. *J. Comput. Chem.* **2013**, *34*, 1819– 1827,DOI: 10.1002/jcc.23323.

3. (a) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **1980**, 58, 1200–1211, DOI: 10.1139/p80-159. (b) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098–3100, DOI: 10.1103/PhysRevA.38.3098. (c) Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822– 8824, DOI: 10.1103/PhysRevB.33.8822.

4. Van Lenthe, E.; Baerends, E. J. Optimized Slater-type basis sets for the elements 1–118. *J. Comput. Chem.* **2003**, *24*, 1142– 1156, DOI: 10.1002/jcc.10255

5. Lenthe, E. v.; Baerends, E. J.; Snijders, J. G. Relativistic regular two-component Hamiltonians. *J. Chem. Phys.* **1993**, *99*, 4597– 4610, DOI: 10.1063/1.466059.

6. Pye, C. C.; Ziegler, T. An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package. *Theor. Chem. Acc.* **1999**, *101*, 396– 408, DOI: 10.1007/s002140050457.

7. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. *J. Phys. Chem.*, **1994**, 98, 11623–11627, DOI: 10.1021/j100096a001.

8. Delferro, M.; Graiff, C.; Elviri, L.; Predieri, G. Self-assembly of polyoxoselenitopalladate nanostars $[Pd_{15}(\mu_3\text{-}SeO_3)_{10}(\mu_3\text{-}O)_{10}Na]^{9-}$ and their supramolecular pairing in the solid state. *Dalton Trans.,* 2010, 39, 4479-4481, DOI: 10.1039/B927537A.

9. See for instance and the references therein: (a) Fernández, J. A.; López, X; Bo, C.; de Graaf, C.; Baerends, E. J.; Poblet, J. M. Polyoxometalates with Internal Cavities: Redox Activity, Basicity, and Cation Encapsulation in $[X^{n+}P_5W_{30}O_{110}]^{(15-n)-}$ Preyssler Complexes, with X = Na^+, Ca^{2+}, Y^{3+}, La^{3+}, Ce^{3+}, and Th^{4+}. *J. Am. Chem. Soc.*, **2007**, 129 (40), 12244–12253, DOI: 10.1021/ja0737321. (b) Cardona-Serra, S.; Clemente-Juan, J. M.; Coronado, E.; Gaita-Ariño, A.; Camón, A.; Evangelisti, M.; Luis, F.; Martínez-Pérez, M. J.; Sesé, J. Lanthanoid Single-Ion Magnets Based on Polyoxometalates with a 5-fold Symmetry: The Series $[LnP_5W_{30}O_{110}]^{12-}$ (Ln^{3+} = Tb, Dy, Ho, Er, Tm, and Yb). *J. Am. Chem. Soc.*, **2012**, 134 (36), 14982–14990, DOI: 10.1021/ja305163t.

10. Baldoví, J. J.; Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Gaita-Ariño, A. Modeling the properties of lanthanoid single-ion magnets using an effective point-charge approach. *Dalton Trans.* **2012**, 41, 13705-13710, DOI: 10.1039/C2DT31411H.

11. Baldoví, J. J.; Cardona-Serra, S.; Clemente-Juan, J. M.; Coronado, E. Gaita-Ariño, A.; Palii, A. SIMPRE: A software package to calculate crystal field parameters, energy levels, and magnetic properties on mononuclear lanthanoid complexes based on charge distributions. *J. Comput. Chem.* **2013**, 34, 1961-1967, DOI: 10.1002/jcc.23341.

12. (a) Rudowicz, C.; Chung, C.Y. The generalization of the extended Stevens operators to higher ranks and spins, and a systematic review of the tables of the tensor operators and their matrix elements. *J. Phys. Condens. Matter* **2004**, 16, 5825-5847, DOI: 10.1088/0953-8984/16/32/018 (b) Rudowicz, C. Transformation relations for the conventional O_k^q and normalised O'_k^q Stevens operator equivalents with k=1 to 6 and -k≤q≤k. *J. Phys. C: Solid State Phys.* **1985**, 18, 1415-1430, DOI: 10.1088/0022-3719/18/7/009; (c) Rudowicz, C. *J. Phys. C: Solid State Phys.* Transformation relations for the conventional *Okq* and normalised *O'kq* Stevens operator equivalents with $k = 1$ to 6 and $-k \le q \le k$. **1985**, 18, 3837, **DOI:** 10.1088/0022-3719/18/19/522.

13. Ryabov, I. D. On the Generation of Operator Equivalents and the Calculation of Their Matrix Elements. *J Magn Reson*. **1999**, 140, 141-145, DOI: 10.1006/jmre.1999.1783.

14. Stevens, K. W. H. Matrix Elements and Operator Equivalents Connected with the Magnetic Properties of Rare Earth Ions. *Proc. Phys. Soc.* **1952**, 65, 209 DOI: 10.1088/0370-1298/65/3/308.

15. Edvardsson, S.; Klinterberg, M. Role of the electrostatic model in calculating rare-earth crystal-field parameters. *J. Alloy. Comp.* **1998**, 275–277, 230-233, DOI: 10.1016/S0925-8388(98)00309-0.

16. Baldoví, J.J; Rosaleny, L. E.; Ramachandran, V.; Christian, J.; Dalal, N. S.; Clemente-Juan, J. M.; Yang, P.; U. Kortz, Gaita-Ariño, A.; Coronado, E. Molecular spin qubits based on lanthanide ions encapsulated in cubic polyoxopalladates: design criteria to enhance quantum coherence. *Inorg. Chem. Front.* **2015**, 2, 893-897, DOI: 10.1039/C5QI00142K.