Supporting Information

SIMDAVIS 1.2: Phosphonates are outstanding SIM ligands. Crown ethers are not.

Walter Cañón-Mancisidor [a,b]*, Christopher Gonzalez Ponce [a], Lorena E. Rosaleny [c] and Alejandro Gaita-Ariño [c]*.

a. University Bernardo O`Higgins (UBO), Faculty of Engineering, Sciences and Technology, School of Engineering, Santiago, Chile. E-mail: walter.canon@ubo.cl.
b. Center for the Development of Nanoscience and Nanotechnology,, CEDENNA, Chile.
c. Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, Valencia, Spain. E-mail: Alejandro.gaita@uv.es.

INDEX

1. What have we changed in the dataset?

The rapid development of synthetic strategies that allow the design of coordination compounds with lanthanide ions and that also have magnetic properties, has generated many compounds in the last three decades. The realization that lanthanide SIMs were not restricted to a single chemical family inspired a large community of chemists to explore different types of compounds, with no single chemical strategy dominating in terms of reported examples.

In a first approximation, of Duan et al. 2022 [1], collected and categorized 1411 compounds that present SIM properties between the years 2003 to 2019, developing a user-friendly dashboard-style web application named SIMDAVIS (Single Ion Magnet DAta VISualisation).

These compounds are organized into 9 chemical families: LnPc2, polyoxometalates (POM), Schiff base, metallocenes, diketonates, radicals, TM near Ln, mixed ligands and other families. In a new review of the systems reported on this platform, we have carefully analyzed the "Mixed Ligands" families with 553 compounds and "Other families" with 202 compounds, to be able to reassign some of the systems reported in those families or to define new families.

2. Classification into chemical families.

The analysis of the structures of the ligands allowed us to reassign: 108 records to the Diketonate family, 35 to Schiff base, 3 to POM and 1 to Metallocene from the Mixed ligands family. Interestingly, the analysis of the samples also allowed us to evidence the presence of two large groups of ligands that were not categorized as a family, due to their chemical similarity as well as their dynamic magnetic response. which defines their SIM properties.

2.1. Phosphonate and derivatives

The first of these new families corresponds to "phosphonate", where the presence of the functional group P=O stands out, with oxygen joining the lanthanide and which presents 54 samples between "Mixed ligands" and "Other families". This family includes all complexes where Ln^{3+} coordinates with at least 2 oxygens belonging to the P=O functional group of a phosphonate, phosphinate or phosphate. In general, these compounds are characterized by the presence of a P-C bond, which has a lower tendency to hydrolysis than the P-O bond and are excellent multidentate ligands due to the three potential coordination oxygens that provide versatility. The most frequent coordination numbers are 6, 7, 8 and 9 with octahedral, bipyramidal pentagonal, triangular dodecahedron and muffin geometries, respectively. Examples for each coordination number are shown in Figure 1 of the main draft.

Table S1. Structural parameters of the Phosphonate family (axial and equatorial P=O distances, only) and showing the U_{eff} values of the reported complexes.

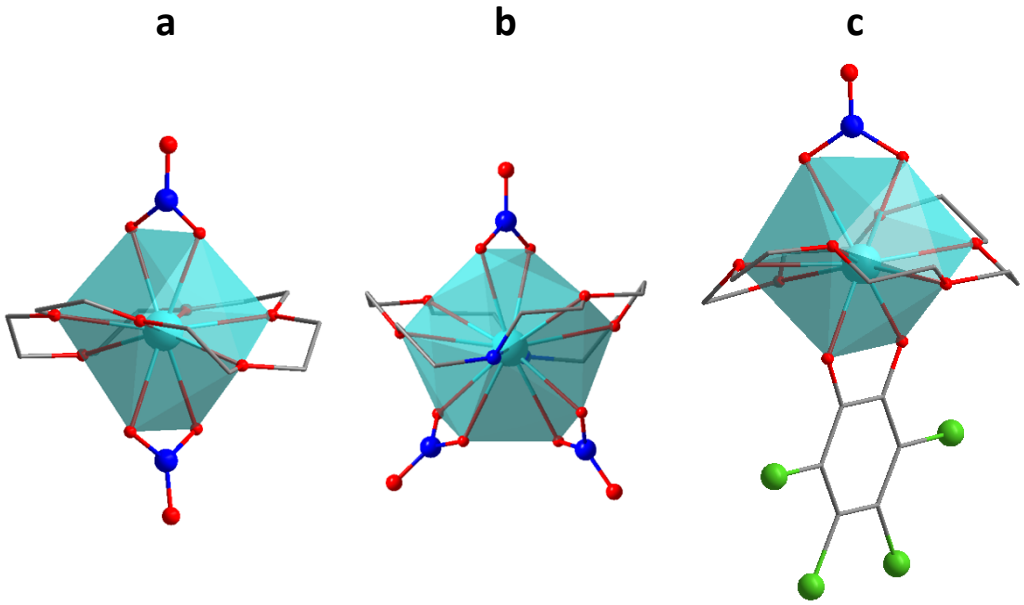
sample_ID	CCDC_COD_ID	NC	Ln^{3+}	U_{eff}	Ln-O(P) axial distances	Ln-O(P) equatorial distances
295	COD7115327	6	Dy	42.9	2.253	2.223; 2.220
375	COD4337817	7	Dy	-	2.296; 2.271	2.276; 2.309; 2.321; 2.330
448	CCDC1035243	8	Dy	32	2.292; 2.472; 2.423	
449	CCDC1035243	8	Dy	29.3	2.292; 2.472; 2.423	
450	CCDC1035242	8	Dy	83	2.287; 2.220; 2.449	
451	CCDC1035242	8	Dy	89.5	2.287; 2.220; 2.449	
540	COD4348425	7	Dy	-	2.257	2.435; 2.263
541	COD4348425	7	Dy	38.2	2.257	2.435; 2.263

572	NA	7	Er	26.8		
680	COD4124922	7	Dy	472	2.218; 2.221	
681	COD4124921	7	Dy	543	2.190; 2.210	
682	COD4124922	7	Dy	474	2.218; 2.221	
683	COD4124921	7	Dy	-	2.190; 2.210	
781	COD1543092	7	Dy	651	2.203; 2.209	
895	CCDC1519259	7	Dy	508	2.217	
896	CCDC1519259	7	Dy	467	2.217	
943	COD4345707	6	Dy	25.2	2.247	2.252; 2.261
944	COD4345707	6	Dy	29.4	2.247	2.252; 2.261
945	CCDC904371	6	Dy	12.6	2.252	2.247; 2.261
1035	CCDC1529266	7	Ho	-	2.199	
1036	CCDC1529266	7	Ho	-	2.199	
1046	CCDC1833630	9	Dy	20.4	2.376; 2.433	2.373
1047	CCDC1833632	9	Dy	-	2.385; 2.447	2.384
1059	COD7121940	7	Dy	460	2.210; 2.228	
1060	COD7121940	7	Dy-Y	-	2.210; 2.228	
1061	COD7121941	7	Dy	600	2.202; 2.209	
1062	COD7121941	7	Dy-Y	-	2.202; 2.209	
1168	NA	7	Nd	-		
1203	CCDC1818726	6	Dy	-		2.235
1208	COD1556607	9	Dy	-	2.278; 2.295	2.283
1209	COD1556608	8	Dy	-	2.248; 2.284	2.284; 2.248
1210	COD1556609	6	Dy	-		2.225; 2.235; 2.287
1211	COD1556610	6	Dy	-		2.231; 2.246
1214	COD4132550	6	Dy	51.2	2.223; 2.224	
1255	CCDC1850934	9	Dy	29.1	2.260; 2.304	2.269
1256	NA	9	Dy	-		
1257	CCDC1850933	9	Dy	-	2.223	2.253
1258	CCDC1850936	6	Dy	-	2.221; 2.224	2.201; 2.191
1259	CCDC1850935	6	Dy	-	2.213	2.315; 2.208
1307	COD7048451	7	Dy	556	2.195; 2.228	
1308	COD7048451	7	Dy	550	2.195; 2.228	
1309	CCDC1884676	8	Dy	40.5	2.279	2.223; 2.220

2.2. Crown Ether

This family includes compounds where the Ln^{3+} ion is coordinated with at least one crown ether ligand and the entire coordination sphere with other small ligands. The crown ether ligands are polydentate heterocycles and are linked through the oxygen atom or some other heteroatom (usually N). The IUPAC nomenclature establishes a system of numbers and letters to indicate the number of atoms in the cycle and the number of heteroatoms in the cycle, the most frequent being 12-C-4, 15-C-5 and 18-C-6, which indicate a heterocycle of 12 atoms with 4 oxygens, 15 atoms with 5 oxygens and 18 atoms with 6 oxygens, respectively. In general, lanthanide complexes with crown ethers have coordination numbers of 8, 9 and 10. Synthetic strategies are based on modifying the size of the corona to generate favorable environments for lanthanide ions, forming

half-sandwich, sandwich and belt-type structures. For this family, the highest U_{eff} value is 75.9 K for a half-sandwich crown ether Dy^{3+} complex with coordination number 10 and a sphenocorona geometry reported by Li et al.[2] Zheng et al. report the synthesis of Dy^{3+} complexes with two equivalents of 12-C-4 to obtain a sandwich-type complex with a biaugmented trigonal prism geometry and a U_{eff} of 63 K [3], as well as the synthesis of belt-type complexes, with the heterocycle in the equatorial plane, giving geometries of sphenocorona and Spherical capped square antiprism. (Figure S1).



	a	b	c
CN	8	9	10
U_{eff} (K)	43	55	NA
τ_0 (s)	1.37×10^{-6}	5.00×10^{-11}	NA
T_B3H (K)	8.2	NA	2.6
Closest Polyedron	square antiprism	muffin	Other
Sample_ID	721	835	1083
CCDC_COD	COD4349107	COD4344989	CCDC1836752

Figure S1. Molecular structures of some representative Ln-Crown ether SIMs and some of their chemical and magnetic descriptors. Colour scheme for atoms: cyan, Ln; grey, C; blue, N; yellow, P; red, O. H atoms are not shown for clarity.

3. Linear Relation of the Chemical Families between the effective magnetic energy barrier and the relaxation time

As one can see in Table S2, the slopes are generally in the range between 1.5 and 3.5, with the exception of the crown ether family. There is a remarkable closeness to a slope equal to 3 in the case of metallocene complexes (2.98), followed by phosphonates (2.94) with every other family presenting deviations of about 10% and above.

Table S2. Fitting of experimental data of $\ln(\tau_0)$ vs $\ln(U_{eff})$ for the all the Chemical Families

	LnPc2	Radical	Other Families	TM near Ln	POM	Schiff Base	Diketonate	Metallocene	Mixed Ligands	P=O	Crown Ether
Intercept	3.6168	107210.4497	361.9649	2745.3790	73.3419	2122.8038	3147.0556	43.7667	1.0537E-05	502.7665	0.0019
Slopes	3.3448	1.7490	2.7032	2.0879	3.4472	2.3513	1.6321	2.9815	1.2406	2.9357	6.5018

References

1 Y. Duan, L. E. Rosaleny, J. T. Coutinho, S. Giménez-Santamarina, A. Scheie, J. J. Baldoví, S. Cardona-Serra and A. Gaita-Ariño, *Nat. Commun.*, 2022, **13**, 7626.

2 F. Gao, F. L. Yang, X. Feng, H. Xu, W. Sun, H. Liu and X. L. Li, *Dalton Trans.*, 2017, **46**, 1317–1323.

3 Y. S. Ding, T. Han, Y. Q. Hu, M. Xu, S. Yang and Y. Z. Zheng, *Inorg. Chem. Front.*, 2016, **3**, 798–807.