Chemical design of molecular nanomagnets using data mining, dashboards, and statistics as a strong framework

C.V. KAVYA SUVARCHALA[1] , Dr V MADHU SUDANAREDDY[2]
Assistant professor[1,2]
DEPARTMENT OF ELECTRONICS AND COMMUNICATION ENGINEERING
P.B.R.VISVODAYA INSTITUTE OF TECHNOLOGY & SCIENCE
S.P.S.R NELLORE DIST, A.P , INDIA , KAVALI-524201

Abstract

After three decades of continuous study, the magnetic memory in molecules has been cooled to the temperature of liquid nitrogen. A smart selection of the magnetic ion and the coordination environment is necessary to increase this operating temperature. But the biggest contributors have been chance, oversimplified ideas, and chemical intuition. We gathered chemical and physical data for lanthanide-based nanomagnets to create a catalogue of over 1400 published experiments, developed an interactive dashboard (SIMDAVIS) to visualize the dataset, and applied inferential statistical analysis to it in order to establish a strong framework for statistically driven chemical design. We discovered that the magnetic memory exhibits a strong link with the effective energy barrier calculated from the Arrhenius equation, and that among all chemical families

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Introduction

With the goal of facilitating the chemical design of lanthanide single-ion magnets (SIMs), herein weminedexperimentaldatafromover450articlesfromthefirst17yearsofSIMresearchandapplieddatavisualizationtoolsfollowedbystate-of-the-artstatisticalanalysis.Thisallowedustoobtainrobuststatistically-driveninsightsonthekeyfactorsgoverningtheslowrelaxationofthemagnetization. Additionally,wecreatedadatasetandadashboard:afreelyaccessibleonlineinteractiveappthatallowsany user to perform qualitative analyses as well as to browse the dataset. This statistical studyrepresents aquantitative and data-supported verification/refutation ofseveral widelyheld "chemicalintuitions"inthefieldofmolecularmagnetism.

A brief history of SIMs

Molecular nanomagnets were reported for the first time at the beginning of the 1990s, when$Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$, a polynuclear magnetic complex with strong magnetic coupling between d-blockionswasreportedtodisplaymagnetichysteresis,similartoclassicalmagnets,butwithaquantumtunnellingmechanismfortherelaxationofthemagnetisation.[1,2]Thiswasthefirstofaplethoraofsingle-molecule magnets (SMMs), the term coined for systems behaving as hard bulk magnets below a certaintemperature, but where the slow relaxation of the magnetization is of purely unimolecular origin. Themagnetic behavior in SMMs can be approximated to that of an effective anisotropic magnetic momentarising from the exchange interactions between the spins of the metal ions. The reversal of this giantanisotropic spin occurs by populating excited spin states and overcoming an energy barrier. Hence, thethermaldependence ofthe relaxationrate was described bythe Arrhenius equation(see Fig. 1), using thiseffective energy barrier (U_{eff}) and a pre-exponential factor (τ_0).[3]Both parameters were not extracteddirectlyfromthe hysteresis loop,but rather fromthe combinedfrequency- andtemperature-dependenceofthe so-1).[3,4]The experimental factthatthemagnetichysteresiswasobservedonlynearliquid-heliumtemperatureswasrationalizedmainlyby the typically low values found for the effective energy barrier $U_{eff} \approx 50$ K.[5]Initial models based oneffective spin Hamiltonians gave rise to the relation $U_{eff} = DS_z^2$ and concluded that the best strategy toraise$U_{eff}$and,therefore,toimprovethemaximumhysteresistemperature(T_{hits}) istomaximizethetotaleffectivespin(S),ratherthanthe magneticanisotropy(D).Indeed,thelatterisalessstraightforward target for the synthetic chemist.[6]Despite great effort toward the synthesis of such systems and anabundanceofmoleculeswithincreasingvaluesofS,very littleprogresswasmadeinthefirstdecadeintermsofincreasing U_{eff}orT_{hits}.[7] Inthe2000s,asecondgenerationofmolecularnanomagnetsemerged,namelybis-phthalocyanines(Pc)“doubledeckers”.[8]Thisnoveltype ofSMMs,commonlyknownasSingleIonMagnets(SIMs),isbasedonmononuclear complexes containing a single magnetic ion embedded in a coordination environment, thusconstitutingthe smallest molecular nanomagnet. Their properties arise fromastrongspinorbit couplingwhich,combinedwiththecrystal-fieldinteractionwiththesurroundingligands,resultsinanenhancedmagnetic anisotropy when compared to the first generation of SMMs. Identical data treatment using theArrhenius equation resulted in effective energy barriers U_{eff} up to an order of magnitude higher for SIMsbasedonrare-earthionswhencomparedtothoseof polynuclearmetalcomplexesofthed-block.

Similarly, the characteristic maximain the out-of-phase component ofthe ac susceptibilityχ'' moved tohighertemperatures,albeittheT$_{hits}$didnotincreasesignificantly.

After the germinal $LnPc_2$, different chemical families such as polyoxometalates[9]and metallocenes[10]were synthesizedandwere shownto exhibit slowrelaxationofthe magnetizationofpurelymolecularorigin(Fig. 2). The realizationthat lanthanide SIMs were not restricted to asingle chemicalstrategyinspiredalargecommunityof chemists.Asaresult,inthelast15years,SIMbehaviorwasreportedinover 600 compounds, whilst above a third of these compounds displayed magnetic hysteresis. Recentefforts have been made to offer some perspective,[11–14]but so many studies pursuing independentinspirations have been reported that it is hard for any single scientist to distinguish anecdotal claimsfromprovenstrategies.Moderntechniquesofdataanalysisandvisualizationcancontributetoremedythis knowledge gap.Inparticular,dashboardsare intuitive graphicalsoftware applicationsfor dynamicdata visualizationandinformationmanagement,ofgrowingpopularityindifferentfields.[15–17]

The present work aims to rationalize the correlations among the different physical variables involved inSIMs. A common working hypothesis is that the parameters arising from the ac magnetometry (e.g., U_{eff})are well correlated with the experimental values (e.g., T_{hits}). This, however, has not been proven and hasactually been challenged in various ways.[14,28,29]Over the years, various theoretical approaches have putthefocusontheroleof differentphysicalprocessesanddifferentparameters.[28–31]Inordertoprovidethesynthetic chemists with a statistically-driven chemical design guide, we applied the techniques of thirdgeneration computational chemistry,[32]starting by collecting a high-quality dataset and representing the datainaninteractivedashboard.

Statistically-driven chemical design of SIMs

SIMDAVISallowsthevisualizationof therelationshipsbetweenchemicalandphysicalvariablesinSIMs,and thereby enables determining the main variables that the synthetic chemist needs to consider toobtain the desired physical properties. We will first analyze this qualitatively employing a series ofboxplots,violinplots andbar charts (see Fig. 4andSupplementaryFigs. 11.1-11.6,12). The fullstatisticalanalysisispresentedin SupplementarySections4,5and6.
First, let us focus on the effective energy barrier U_{eff} and the blocking temperature T_{B3} (the temperatureformaximumout-of-phaseacsusceptibilityχ''at10^3Hz,seeFig.1).FromFig.4andSupplementaryFigs.11.1-11.4,wecanseethattheonlychemicalfamilywithaclearly distinctbehavioristhe$LnPc_2$family,with median values of U_{eff} > 300 K and T_{B3} > 30 K. Equivalently, one can see that Dy^{3+} and Tb^{3+} aresomewhat better than the rest, and that in general oblate ions perform better than prolate ions, for bothproperties. Inaddition, non-Kramer's ions present higher medianT_{B3}but similar U_{eff}values comparedwithKramer'sions.

Now, let us analyse the maximumhysteresis temperature T_{hits}whichhas beenmuchless studieddespitebeing the main justification for this whole field. The only chemical family with a distinct positivebehavior is the metallocene family. More surprisingly, Er^{3+} complexes have distinctly high hysteresistemperatures,markedlywithahighermedianthanDy^{3+}orTb^{3+}complexes.Thisisinsharpcontrastwiththeir relative T_{B3} values which are consistently much lower in the case of Er^{3+} complexes. This not onlyindicates that searching for equatorial environments, precisely the ones that favor good magneticproperties in Er^{3+} complexes,[30]often results in more rigid ligands, but also indicates an underexploredterritory.Itiscertainly possiblethatchemicalmodificationsof$[Er(COT)_2]^-$(orotherEr^{3+}record-bearing complexes) designedtooptimizethedetrimentaleffectofmolecular vibrationsmay achieverecordsthatarecompetitivewith$DyCp_2$.Prolateionsareconsistently-andsurprisingly-betterthantheoblateones,having a higher median value for T_{hits}. This is again in contrast with the opposite behavior which isobservedforT_{B3}andU_{eff},andpossiblyagainduetotheinfluenceofEr^{3+}complexeswiththeirmorerigidequatorial environments. Finally, the coordination number and the number of ligands does have aninfluence on the statistically expected hysteresis temperature, with the best ones being 2 and 7 in thecaseofthecoordinationnumberandjust7forthenumberofligands.Aswewilldiscussbelow,therearechemicalinsightstobegained fromthis.

Toputallthesetrendsintoperspective,itisimportanttonumericallyanalysetheconnexonbetweenthedifferent variables andthe clusteringofour data. A lognormalanalysis (see SupplementarySection4.3)shows that the three mainchemicalvariables, namelythe chemicalfamily, the lanthanide ionand thecoordinationelements,aresufficienttoreasonably explainthevariationofvaluesoftheothers,meaningthereisalimitontheinformationonecanindependentlyextractfromtherestof thechemicalvariables.Multiple correspondence analysis (see SupplementarySections 4.1,4.2)suggests achemicalclusteringthat consists in three small groups, namely Gd^{3+} complexes, metallocene's and LnPc$_2$ double deckers,and two much larger groups with a large overlap with oblate and prolate ions respectively. A factorialanalysis ofmixeddataconsideringalsoallmagnetic informationavailable (see SupplementarySection6) simplifies the clustering to three groups. Again, the two distinct families present a large overlap withmetallocene's and LnPc$_2$ double decker chemical families, both of them presenting significantly better propertiesthantheotherkindsofsamples.

Further insight is provided bybar charts representing the reported presence ofmagnetic hysteresis,whetherfullorpinched,asafunctionofdifferentchemicalvariables(Fig.4).Notethatwearelimitedbytheminorityofthesampleswherehysteresisoritsabsenceisreported;inthevastmajorityofthecasesthisinformationislacking.Nevertheless,hereitisapparentthatcertainfamiliessuchasLnPc$_2$(andmetallocene's)tendtodisplay(pinched)hysteresis.

The effective energy barrier: oversimplified yet meaningful

A key question is how much the analyses in this field have been affected by the simplified assumptionthatSIMsrelaxviaanOrbachmechanism, whichischaracterizedby$\tau_0$andU_{eff}.Ithasbeenpointed outthat frequently, as U_{eff} increases, τ_0 decreases, leaving relaxation times essentially constant.[5]Theclassicaltextof AbrahamandBlaneyofferedthefollowingrelationbetweenthetwoparametersforthetwo-phononOrbachprocess:[34]

$$\frac{1}{\tau_0} = R_{\mathrm{Or}} \cdot (U_{\mathrm{eff}})^n \tag{1}$$

where n = 3, reasonable parameters for rare earth elements resulted in an Orbach rate $R_{Or} \approx 10^4$ K^{-3}·s^{-1},andearlyexperimentalresultswereintherange10^{3}K^{-3}·s^{-1}<R_{Or}<10^{5}K^{-3}·s^{-1}.Fitting$\tau_0$vsU_{eff}inourdataset to equation (1) results in n ≈ 2.4, $R_{Or} \approx 10^3$ K^{-3}s^{-1} (see Supplementary Table 5). This minordiscrepancy with the expected exponent serves as an independent evaluation of the limitations of asimple Orbach model. We also find R_{Or}(prolate) ≈ 5·R_{Or}(oblate), meaning that, for comparable U_{eff},relaxationforoblateionsisonaveragesubstantiallyslowerthanthatforprolateions.Thisisconsistentwith the observation that complexes of oblate ions present values of T_{B3} higher than expectedconsideringtheirU_{eff}(seeSupplementaryFig.11.3).Thelimited(<100)datapointsof$U_{eff,ff}$,$\tau_{0,ff}$pairs, whereallrelaxationprocesseswereconsidered,presentabetteragreementontheexponent,withn≈3andlowerOrbachratesR_{Or}≈150K^{-3}s^{-1}.
Theremainingcrucialissueistoquantifyuptowhatlevelthevalueof$U_{eff}$and$\tau_0$arewellcorrelatedwiththe slow relaxation of the magnetisation, or to determine whether one would need to employ $U_{eff,ff}$instead. Let us proceed with increasing the order of complexity. A visual inspection in SIMDAVIS showsthat,inafewcaseswherethereissimultaneousinformationon$U_{eff}$and$U_{eff,ff}$,theirvaluesareverysimilar(Fig. 5a). Furthermore, this partial information is corroborated by the very similar dependencies of T_{B3} orT_{hyst}vs either U_{eff}or $U_{eff,ff}$, as wellas inthe numericalcorrelations (see SupplementarySections 3.2 and5.3). A categorical analysis (Figs. 5b, c) shows that the data dispersion is large, meaning that it isimpossibletopredicttheexperimentalbehaviourforanindividualsamplemerelyfromitsU_{eff}value. However,itdemonstratesthat,statistically,sampleswhichpresentamaximumintheout-of-phasesusceptibilityχ'', or hysteresis, also present higher U_{eff}values. A more thoroughnumericalanalysis (seeSupplementarySection6)confirmsthesetrends.

Anin-depthstatisticalanalysisofallphysicalparametersbasedontheAkaikeInformationCriterion(seeSupplementarySection5.3)concludesthatU_{eff}derivedfromasimpleArrheniusplotisthebestsinglepredictorforthemagneticbehaviourinourdataset.Thismeansthat,whetherwearediscussingintermsofthe out-of-phase component ofthe ac susceptibilityor magnetic hysteresis, $U_{eff}$is a better predictorthan τ_0, $\tau_{0,\ ff}$, $U_{eff,2}$ and, in practice, than $U_{eff,\ ff}$. Factorial analysis of mixed data (see SupplementarySection 6) also reveals the predictive power of U_{eff} compared with τ_0. Note that this does not contradictpreviousstudieswhichdemonstratedthatavariationintheOrbachbarrierdoesnotfullyexplainthedifferencesinretentionof magnetisation,[14]sincewehavenotexplicitlyconsideredotherrelaxationmechanismsinthepresentwork.temperatures. It is possible that the next family of record-setters is related to one of the promisingcandidates in Fig. 6. Two axial phosphine oxide ligands with bulky substituents seem to function in asimilarwayasmetallocene's,despitethefiveequatorialH_2Omolecules.[24,37]Thisstrategyisnotrestrictedto phosphine oxides and deserves to be explored further: as can be seen in Supplementary Fig. 11.4,complexeswith7ligandshavemedianvaluesofT_{hyst}closeto10K,ashighasthosewith2ligands.

Atthesametime,hereweprovideacatalogueof lanthanideSIMs,togetherwithSIMDAVIS,adashboardthat allows its interactive navigation; this is a type of tool utterly missing in the field of molecularnanomagnets. Perhaps more importantly in the wider perspective of design of new materials[38–40]andnewmolecules,[32,41]thedatasetcuratedinthisworkwillserveforMachineLearningstudiesandcanalsobe employed as an annotated training data set for the development of new web scraping systems toretrieve chemical data,[42,43]or even word embeddings,[44]from the scientific literature. Finally, this workconstitutes a step towards the availability of findable, accessible, interoperable, and reusable (FAIR) datainChemistry.[45]

METHODS

Data gathering.

This process started with the collection and organisation of literature data. The following search criterion was applied for the manuscript: articles are searched via Web of Science, employing this code:

TOPIC: TS=((lanthan* OR 4$f OR "rare$earth") AND ((single NEAR/1 magnet*) OR "slow relaxation"))Timespan:2003-2019
For an article to be included in the study, it needs to contain data on at least one compound with certainrequirementsasfollows:(a)containonetrivalentlanthanideionfromthesetLn={Pr,Nd,Sm,Gd,Tb,Dy, Ho, Er, Tm, Yb} and (b) contain no other paramagnetic entity with the only accepted exception being thepresenceofasingleradicalinthecoordinationsphereand(c)presentnostrongLn-Lninteraction,inparticular meaning the Ln-Ln distance needs to be larger than 5 Å and more than 3 bridging atomsbetweenneighbouringLncentres,andtherecannot bearadicalinthebridge.Additionally,thedataneedstoincludeatleastoneofthefollowinginformation:(a)whether χ''presentsamaximumasafunctionofT, or a mere frequency-dependence, or neither; (b)χ'' vs Twith at least one frequency(f)in the window 0.9kHz ≤ f ≤ 1.1 kHz and at a field (B) in the window 0 ≤ B ≤ 2 T; (c) U_{eff}; (d) the presence or absence ofhysteresis; (e) T_{hyst} at sweep speeds (v) in the window 0.05 T/s ≤ v ≤ 0.3 T/s. The compounds wereclassifiedinchemicalfamilies:$LnPc_2$,polyoxometalates,Schiffbase,metallocenes,diketonates,radicals,TM near Ln, mixed ligands, and other families. Furthermore, we registered for each sample (whenavailable), the lanthanide ion, its concentration, the coordination number and number of ligandscoordinatedtothelanthanideions,thecoordinationelements,thepresenceofafield-dependentχ''oramaximum, the temperature of said maximum in presence or absence of an external magnetic field, theexternalmagneticfield,theextractedeffectiveenergybarrierandrelaxationtime,eitherfromasimplifiedArrheniusfitorfromamodelconsideringallrelaxationprocesses,whetherthesewereextractedfromthemaxima of χ'' vs T at different frequencies or from an Argand fit, the presence of hysteresis in themagnetisation, and the maximum temperature at which it was recorded. Additionally the DOI, the fullreference to the original article, and a link to a CIF file were recorded for each sample. Further detailsincluding the classification in chemical families and the criteria for data extraction are provided inSupplementarySections1and 2.

SIMDAVIS dashboard. We programmed the dashboard using R language 51,52 and shiny, 53 an open-source R package to create the interactive web app. The design aimed to obtain a clean and simple user interface that adapts automatically to any screen size. The R packages read, 54 dplyr, 55 DT, 56 ggplot2 57 and rcrossref 58 were also employed in the development of the dataset or the app. The dashboard-style web application is available at https://go.uv.es/rosaleny/SIMDAVIS. This interface allows for variables in the analysis, and subsets of the data, to be adjusted and chosen in real time.

Statistical analysis. The statistical analysis was also based on R, a widely used software environment for statistical computing and graphics, and included the Gifi system for Multiple Correspondence Analysis 59 (R homals package, 60 ade4 package, 61 see details in Supplementary Section 4.1), hierarchical clustering studies (FactoMineR, 62 see details in Supplementary Section 4.2), lognormal modelling (Poisson's distribution, see Supplementary Section 4.3), factorial analysis of mixed data (FactoMineR and factoextra, 63 see details in Supplementary Section 6) as well as Pearson's product-moment correlation and the Akaike information criterion (AIC) 64 (see details in Supplementary Section 5.3). The analysis was repeated and verified an overall excellent qualitative and quantitative consistency in all results between the period 2003-2017 (1044 samples) and 2003-2019 (1405 samples).

Program of Excellence and CDEIGENT/2019/022). The statistical analysis was performed by RaquelGavidiaJosawiththeStatisticalSectionoftheS. C.S.I.E.(UniversitatdeValència).TOCfigurecreated withBioRender.com.

Results

An interactive dashboard for lanthanide SIMs

In this work, we built a dataset of the most relevant chemical and physical properties of 1405 lanthanide SIM samples collected from 451 scientific articles (Supplementary Section 7) published between 2003 and 2019 and developed a user-friendly dashboard-style web application named SIMDAVIS (Single Ion Magnet DAta VISualization) to host it. The dataset contains over 10000 independent pieces of chemical information, as well as over 5000 independent pieces of physical (magnetic) information. Furthermore, the dataset is hierarchically clustered into magnetostructural “taxonomies” (see Supplementary Sections 4 and 6) in order to pave the way for further analysis, including Machine Learning studies. SIMDAVIS allows the chemical community to visualize the key relationships between chemical structures and physical properties in our catalogue of SIMs. Our interactive dashboard can be directly invoked by accessing the internet site where it is located. 33 It is organized in 6 main tabs: Home, ScatterPlots, BoxPlots, BarCharts, Data (View Data and Download Data) and About SIMDAVIS (Variables, Authors, Feedback&Bugs, Changelog and License) as we can observe in Fig. 3. In the SIMDAVIS dashboard, the most versatile source of graphical information is the “ScatterPlots” tab,. The next two tabs display the data in complementary ways. The “BoxPlots” tab allows to examine the distribution of each SIMs quantitative property vs a categorization criterion, e.g. we can see the distribution of Ueff values as a function of the coordination elements. The boxplot for each category is shown, including the median and the interquartile range. The “BarCharts” tab allows the exploration of the frequency of different qualitative variables in our dataset. Stacked bar graphs allow the simultaneous analysis of two qualitative variables, e.g. we can display, for each chemical family, the number of samples which present magnetic hysteresis. The “Data” tab is a powerful interface to browse the dataset, featuring the possibility to choose the data columns to show, ordering in ascending or descending order, and filtering by arbitrary keywords; it also permits downloading all data, including links to the CIF files, when available. Finally, the “About SIMDAVIS” tab contains information about the variables contained in the dataset.

Conclusions

We have systematically analysed over 450 articles to collect information from over 1400 samples reported over the first 17 years of the field of lanthanide-based SIMs and built a user-friendly dashboard for the visualization of all the collected data. Moreover, we carried out an in-depth statistical analysis that allowed extracting trends, distinguishing the most relevant variables and grouping the data in clusters based on their chemical and physical properties. From this study, we can highlight two main pieces of information. In the first place, from the point of view of the parametric characterisation, the simple Arrhenius fit assuming an Orbach process has been proven to be surprisingly meaningful, with the expected relation between τ0 and Ueff . One can therefore perform this oversimplified theoretical fit knowing that the effective energy barrier Ueff has been proven to present a consistently good correlation with SMM behaviour. Crucially, we have also shown the very different nature of short-term magnetic memory in form of the blocking temperature TB3 at 10 3 Hz and its long-term counterpart in the form of maximum hysteresis temperature Thyst . The best strategies that optimize the former are not necessarily the best for the latter. In the second place, the chemical roadmap for the preparation of lanthanide complexes with higher Thyst becomes now a little clearer. There is a single chemical strategy that consistently produces good magnetic memories, namely sandwiching an oblate ion between two rigid, planar, aromatic ligands; furthermore, the ion should be chosen to result in the most favourable MJ structure, given the electron distribution offered by the ligand. Up to now, only two chemical families are well adapted to this strategy, namely TbPc2 complexes and dysprosium metallocenes.

Optimization is ongoing within these two families, for example TbPc2 complexes featuring a radical Pc display enhanced properties, 35 and the reduced (divalent) analogues of DyCp2 . 36 We find comparatively little value in further pursuing chemical strategies that have been amply explored and never yielded hysteresis above 10 K. On the other hand, we also evidence that there is, of course, value in chemical ingenuity and exploration, in the quest for another successful strategy, which according to our results might well be based on equatorial erbium complexes, since these display consistently high Thyst values. Note that a few complexes included in our data fall into ample families such as “mixed ligands” or “other families”, and yet present excellent hysteresis Page 8/19 temperatures. It is possible that the next family of record-setters is related to one of the promising candidates in Fig. 6. Two axial phosphine oxide ligands with bulky substituents seem to function in a similar way as metallocenes, despite the five equatorial H2O molecules. 24,37 This strategy is not restricted to phosphine oxides and deserves to be explored further: as can be seen in Supplementary Fig. 11.4, complexes with 7 ligands have median values of Thyst close to 10 K, as high as those with 2 ligands. At the same time, here we provide a catalogue of lanthanide SIMs, together with SIMDAVIS, a dashboard that allows its interactive navigation; this is a type of tool utterly missing in the field of molecular nanomagnets. Perhaps more importantly in the wider perspective of design of new materials 38–40 and new molecules, 32,41 the dataset curated in this work will serve for Machine Learning studies and can also be employed as an annotated training data set for the development of new web scraping systems to retrieve chemical data, 42,43 or even word embeddings, 44 from the scientific literature. Finally, this work constitutes a step towards the availability of findable, accessible, interoperable, and reusable (FAIR) data in Chemistry. 45

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