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Impact of Coordination Environment on Magnetic Properties of Single-Molecule Magnets Based on Homo- and Hetero-Dinuclear Terbium(III) Heteroleptic Tris(Crownphthalocyaninate)

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A series of Tb\textsuperscript{III} triple-decker heteroleptic crownphthalocyaninate complexes consisting of a homodinuclear compound [(15C5)\textsubscript{3}Pc\textsubscript{2}Tb(15C5)\textsubscript{3}Pc]Tb(Pc) (1) and two novel heterodinuclear compounds [(15C5)\textsubscript{3}Pc\textsubscript{2}Tb(15C5)\textsubscript{3}Pc]Y(Pc), (2), and [(15C5)\textsubscript{3}Pc\textsubscript{2}Y(15C5)\textsubscript{3}Pc]Tb(Pc) (3), have been synthesized. All compounds were characterised using UV-Vis spectroscopy, HR-ESI-MS, MALDI-TOF-MS, and \textsuperscript{1}H NMR Spectroscopy, followed by exploration into the effects of lanthanide coupling and ligand field symmetry on the magnetic properties of these complexes using SQUID magnetometry. Magnetic measurements on the homonuclear Tb\textsuperscript{III} complex (1) displayed non-negligible ferromagnetic coupling between magnetic ions, eliciting a high zero-field energetic barrier to magnetic relaxation of $U_{\text{eff}} = 229.9(0)$ K, while the heteronuclear Tb\textsuperscript{III}/Y\textsuperscript{III} complexes displayed single-ion field-induced slow relaxation of the magnetization; yielding energetic barriers of $U_{\text{eff}} = 129.8(0)$ K for 2, and 169.1(8) K for 3.

Introduction

Single-Molecule Magnets (SMMs) are unique molecular entities capable of exhibiting slow relaxation of the magnetisation below a certain blocking temperature. These systems are continuously being improved through careful synthetic design strategies in order to achieve higher energy barriers to magnetic relaxation ($U_{\text{eff}}$), and higher magnetic blocking temperatures ($T_B$). Since SMMs exhibit clean quantum behaviour\textsuperscript{1} they are appealing candidates for application in molecular electronics.\textsuperscript{2,3} Thus, magnetochemists design and promote SMMs with the goal of achieving breakthroughs in information storage,\textsuperscript{4} quantum computing,\textsuperscript{5-10} and molecular spintronics applications,\textsuperscript{2,11-16} among others. There is extensive interest in new synthetic approaches to further understand these systems, and advance them toward a niche within various high-density electronics applications.

Rare-earth-based systems are currently the benchmarks within molecular magnetism due to their large magnetic moments arising from unpaired $f$-electrons, and more importantly their inherent magnetic anisotropy. Very recently a new benchmark was set by a Dy\textsuperscript{III}-based SMM, which displayed a $T_B = 20$ K.\textsuperscript{17} This was an incredibly significant discovery within the field of molecular magnetism, as the previous record was set in 2011 by a homonuclear Tb\textsuperscript{III} dimer, where the paramagnetic ions were coupled through a dinitrogen radical bridging moiety ($T_B = 14$ K).\textsuperscript{18} Interestingly, the other benchmark within the SMM field was set in 2013 by a heteroleptic Tb\textsuperscript{III} phthalocyanine (Pc) complex, with $U_{\text{eff}} = 652$ cm\textsuperscript{-1} (938 K, at $T_m = 58$ K).\textsuperscript{19} Thus, Tb\textsuperscript{III} systems have clearly proven to be worthy of great interest to the magnetic community. In particular, extensive work has been performed on synthesizing and studying the magnetic properties of homoleptic and heteroleptic Tb\textsuperscript{III} sandwich phthalocyanine systems ever since they were first reported by Ishikawa in 2003.\textsuperscript{20} These systems possess a $D_{4d}$ 4-fold axial symmetry, which promotes the substantial orbital contribution from the single Tb\textsuperscript{III} ion to be axially aligned, thus creating a large separation of states (large $U_{\text{eff}}$ value). Besides their tendency towards high energetic barriers to magnetic relaxation, they have also been shown to be synthetically customizable for surface adhesion.\textsuperscript{21} Thus, these systems are promising candidates for the aforementioned electronics applications; as SMMs will inevitably be necessitated to operate magnetically upon surface adhesion in order to be viable candidates.\textsuperscript{21}

Due to the coordinatively-induced axiality of the orbital component within sandwich tetrapyrrolic compounds, interest is now being directed toward the investigation of $f$-$f$ interactions. To this end, Ishikawa’s group has demonstrated...
that Tb\textsuperscript{III} ions in a series of isomeric triple-decker phthalocyaninato-porphyrinato complexes display distinctly different magnetic behavior, depending on the symmetry of the coordination polyhedron.\textsuperscript{22} The nature of peripheral substituents on sandwich phthalocyanines can significantly impact the structural properties, such as the tilt and twist angles of decks, as well as interplanar and M-M distances.\textsuperscript{23} Thus, varying substituents on the ligand architecture, the magnetic properties of the complex are undoubtedly impacted. The impact of such substituents on the magnetic behavior of Tb\textsuperscript{III} within sandwich phthalocyanines can be uniquely studied through magnetic isolation of the paramagnetic ion with a diamagnetic cation; for example Y\textsuperscript{III}. This method involves the isolation of three dimeric complexes: Tb\textsuperscript{III}/Tb\textsuperscript{III}, Tb\textsuperscript{III}/Y\textsuperscript{III} and Y\textsuperscript{III}/Tb\textsuperscript{III}; thus allowing for the magnetic ion to be isolated in each pocket/deck and separately studied.

Interestingly, only two previous examples of heteroleptic triple-decker Tb\textsuperscript{III}-based complexes have been synthesized and magnetically studied in this manner.\textsuperscript{22,24} In each case, triple-decker complexes were synthesized with two unsubstituted Pc ligands, and one substituted Pc/Por ligand decorated with electron donating groups. In the first study the electron donating group was OMe, where both the heteroleptic and homoleptic Ln coordination environments were square antiprismatic (SAP).\textsuperscript{24} Conversely, in the more recent study the homoleptic (unsubstituted Pc) pocket was SAP, whereas the pocket with the OMe-substituted Por ligand was square prismatic (SP).\textsuperscript{22} Interestingly, magneto-structural correlations were thoroughly explored for each coordination environment in this system; finding that the SAP coordination environment elucidated slower magnetic relaxation in Tb\textsuperscript{III}.\textsuperscript{22} Furthermore, the SP ion in the Tb\textsuperscript{III}/Tb\textsuperscript{III} complex was found to speed up the overall relaxation of the SAP Tb\textsuperscript{III} ion. Thus, through selectively isolating the magnetic Tb\textsuperscript{III} ion in each deck they were able to elucidate the effects of their substituent and the resulting coordination environment on the magnetic behavior of the Tb\textsuperscript{III} ion in a heteroleptically substituted pocket.

We sought to build on the previous work performed on Tb\textsubscript{2}Pc\textsubscript{2} systems by employing new design strategies toward the fundamental study of ligand substituent effects on the promotion of stronger 4f coupling and thus better magnetic properties. Since the record for the highest energy barrier is homonuclear and two novel heteronuclear triple-decker complexes with unsubstituted phthalocyanine and crown-phthalocyanines as ligands (Fig. 1):

\begin{equation}
[(15C5)\text{Pc}]Tb[(15C5)\text{Pc}]Tb(\text{Pc})
\end{equation}

(1),

\begin{equation}
[(15C5)\text{Pc}]Tb[(15C5)\text{Pc}]Y(\text{Pc}),
\end{equation}

(2), and

\begin{equation}
[(15C5)\text{Pc}]Y[(15C5)\text{Pc}]Tb(\text{Pc})
\end{equation}

(3).

In order to facilitate these goals we synthesized one homonuclear and two novel heteronuclear triple-decker complexes with unsubstituted phthalocyanine and crown-phthalocyanines as ligands (Fig. 1):

\begin{equation}
[(15C5)\text{Pc}]M(15C5)\text{Pc}
\end{equation}

Experimental

Materials and methods

Commercial 1-chloronaphthalene (1-CIN) (Acros Organics) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich) were used as received. Reagent grade chloroform was dried and distilled from CaH\textsubscript{2}. Methanol (Merck) was dried over 4 Å molecular sieves. Diphthalocyaninolanthanum La(Pc)\textsubscript{2},\textsuperscript{27,28} di-tetra-15-crown-5-phthalocyaninates M[(15C5)\text{Pc}],\textsuperscript{29} H\textsubscript{3}[(15C5)\text{Pc}]\textsuperscript{30} and acetylacetonates M(acac)\textsubscript{3}\textsubscript{,}\textsuperscript{31} M = Tb,Y were prepared by previously published procedures. Column chromatography was performed on neutral Al\textsubscript{2}O\textsubscript{3} (Merck, II-III Brockman activity).

UV-Vis absorption spectra were recorded on a Cary-100 Varian spectrophotometer in 10-mm quartz rectangular cells. The \textsuperscript{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz with internal deuterium
lock at room temperature. The proton chemical shifts (δ, ppm) were referenced to the residual proton signals (δ=7.26 ppm) in CDCl₃, which was employed as solvent. High-resolution mass spectra (HRMS) were recorded on an Orbitrap ESI-TOF mass spectrometer. Positive-ion MALDI TOF mass spectra were run on Bruker Daltonics Ultraflex spectrometers using a reflector mode with a 20 mV voltage at the target. 2,5-Dihydroxybenzoic acid was used as the matrix.

Magnetic measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL7, operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 5 T. Susceptibility measurements were performed on powdered samples of the following amounts: 9.5 mg 1, 18.9 mg 2, and 33.7 mg 3, each wrapped within a polyethylene membrane. Direct current (dc) susceptibility measurements were performed at 1000 Oe, and alternating current (ac) susceptibility measurements were performed under an oscillating ac field of 3.78 Oe, with ac frequencies ranging from 0.1-1500 Hz. Samples 2 and 3 did not exhibit a strong zero-field ac signal, and thus were measured under an optimized applied dc field of 1500 Oe. The magnetization data was initially collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples.

Synthetic procedures

[(15CS)₄Tb][15CS₄]PcTb(Pc)[Tb⁺,Y⁺] (1). A mixture of La(Pc)₃ (55.0 mg, 47 μmol), H₂[15CS₄]Pc (60 mg, 47 μmol) and Tb(acac)₃·H₂O (67 mg, 141 μmol) was dissolved under sonication in 20 ml of 1-chloronaphthalene and refluxed under a slow steam of Ar for 20 min until no further changes in the UV-Vis spectrum of the reaction mixture were observed. After cooling to room temperature, the mixture was transferred to a chromatographic column packed with neutral alumina in CHCl₃. Multiple gradient elution with CHCl₃:1.25 vol.% MeOH and evaporation of solvents afforded target complex as a dark-blue solid (59 mg, 82%).

UV-Vis (λ max nm (r.u.)): 702(0,17), 641(1), 349(0,62), 292(0,5).

HR-ESI: found 1124.98114 - [M+3Na]⁺, calculated for [C₃₆H₃₆N₅O₄Tb+3Na]⁺ - 1124.975

[^H-NMR, CDCl₃, δ ppm: -154.91 (br s, 8H, H₆⁺), -68.91 and -66.34 (2s, 2×8H, H₆⁻), -55.45 and -54.38 (2s, 2×8H, H₂⁺), -36.86 and -36.03 (2s, 2×8H, 2′-CH₂⁺), -34.66 (6s, 8H, β-H_, H₂⁻), -33.15 (5s, 8H, 1-CH₂⁻), -22.32 and -21.98 (2s, 2×8H, 3′,3′-CH₂⁻), -18.76 and -18.47 (2s, 2×8H, 4′-CH₂⁻), -17.87 (5s, 8H, 1′-CH₂⁺), -15.35, -11.46, -10.30, -7.40, -6.60, -6.40 (2s, 6×8H, 2′,2′,3′,3′,4′,4′-CH₂⁻).

[(15CS)₄Pc][15CS₄]Pc[Y(Pc)[Tb⁺,Y⁺] (2). A mixture of Tb[15CS₄]Pc₂ (60 mg, 22 μmol), La(Pc)₃ (26.4 mg, 22 μmol) and Y(acac)₃·H₂O (27 mg, 66 μmol) was dissolved under sonication in 20 ml of 1-chloronaphthalene and refluxed under a slow steam of Ar for 15 min, until no further changes in the UV-Vis spectrum of the reaction mixture were observed. After cooling to room temperature, the mixture was transferred to a chromatographic column packed with neutral alumina in CHCl₃. Multiple gradient elution with CHCl₃:1.25 vol.% MeOH and evaporation of solvents afforded target complex as a dark-blue solid (59 mg, 82%).

UV-Vis (λ max nm (r.u.)): 702(0,21), 641(1), 349(0,62), 292(0,5).

HR-ESI: found 1124.98114 - [M+3Na]⁺, calculated for [C₃₆H₃₆N₅O₄Tb+3Na]⁺ - 1124.975

[^H-NMR, CDCl₃, δ ppm: -154.91 (br s, 8H, H₆⁺), -68.91 and -66.34 (2s, 2×8H, H₆⁻), -55.45 and -54.38 (2s, 2×8H, H₂⁺), -36.86 and -36.03 (2s, 2×8H, 2′-CH₂⁺), -34.66 (6s, 8H, β-H_, H₂⁻), -33.15 (5s, 8H, 1-CH₂⁻), -22.32 and -21.98 (2s, 2×8H, 3′,3′-CH₂⁻), -18.76 and -18.47 (2s, 2×8H, 4′-CH₂⁻), -17.87 (5s, 8H, 1′-CH₂⁺), -15.35, -11.46, -10.30, -7.40, -6.60, -6.40 (2s, 6×8H, 2′,2′,3′,3′,4′,4′-CH₂⁻).

[(15CS)₄Pc][15CS₄]Pc[Y(Pc)[Y⁺,Tb⁺] (3). A mixture of Y[15CS₄]Pc₂ (60 mg, 22 μmol), La(Pc)₃ (26.4 mg, 22 μmol) and Tb(acac)₃·H₂O (28 mg, 68 μmol) was dissolved under sonication in 20 ml of 1-chloronaphthalene and refluxed under slow steam of Ar for 20 min until no further changes in the UV-Vis spectrum of the reaction mixture were observed. After cooling to room temperature, the mixture was transferred to a chromatographic column packed with neutral alumina in CHCl₃. Multiple gradient elution with CHCl₃:1.25 vol.% MeOH and evaporation of solvents afforded target complex as a dark-blue solid (59 mg, 82%).

UV-Vis (λ max nm (r.u.)): 702(0.21), 641(1), 349(0.62), 292(0.5).

HR-ESI: found 1124.974 - [M+3Na]⁺, calculated for [C₃₆H₃₆N₅O₄Tb+3Na]⁺ - 1124.975

[^H-NMR, CDCl₃, δ ppm: -71.02 and -69.27 (2s, 2×8H, H₆⁺), -33.71 (5s, 8H, 1′-CH₂⁺), -29.27 (5s, 8H, 1′-CH₂⁻), -22.11 (5s, 8H, 1-CH₂⁻), -19.22 (8s, 8H, 1-CH₂⁻), -15.42 (8s, 8H, 2-CH₂⁻), -11.02 (8s, 8H, 2′-CH₂⁻), -10.37 (8s, 8H, 2′-CH₂⁺), -8.22 (8s, 8H, β-H_, H₂⁻), 24.56 (8s, 8H, α-H₁⁻)

Results and Discussion

Synthesis and Structural Characterization

The synthetic approach toward complexes 1-3 was motivated by a desire to obtain isostructural homonuclear and heteronuclear complexes containing paramagnetic Tb³⁺ and diamagnetic Y₃⁺ atoms in an SAP coordination environment. The homonuclear complex (1) was prepared as previously described. Reported methods of preparation of heteronuclear trisphthalocyaninates utilize a "raise-by-one-story" strategy, where a monophthalocyaninate is added to a double-decker phthalocyaninate complex containing a different metal. Conversely, herein we used another approach to synthesize heteronuclear trisphthalocyaninates, which was previously developed for the preparation of heteronuclear Yb/Y triple-decker phthalocyaninates. This approach includes the use of La(Pc), as an efficient and convenient source of Pc²⁻ dianion. Indeed, the reaction between Tb[(15CS)₄Pc]₂ and La(Pc)₃, in the presence of Y(acac)₃, under reflux in 1-chloronaphthalene, afforded the heteronuclear complex [(15CS)₄Pc][Tb[(15CS)₄Pc]Y(Pc) (2), which was isolated in 82% yield. Remarkably, the reaction rate was exceptionally high; only 15 min were required for complete conversion of the starting double-decker into the target heteronuclear compound. The isomeric complex, [(15CS)₄Pc][Tb[(15CS)₄Pc]Pc(Pc) (3), was prepared in the same
manner, and was isolated in 78% yield. After column chromatographic purification on alumina, bulk purity of all complexes was investigated and structural characterization were performed.

The UV-Vis spectra for 1-3 (Fig. S1-S3) are typical for triple-decker complexes; displaying the N-band (~292 nm) and the bathochromically shifted broad Soret band (343-349 nm), which is characteristic of the positioning and number of electron donating crown-ether substituents. Furthermore, we also observe the lanthanide-dependent Q-band at 642 nm; which experiences a hypsochromic shift and splitting upon decreasing ionic radii of the metals (the Q-band is located at 698 nm for 1 and is shifted to 702 nm for heteronuclear 2 and 3).33,34,35,36

Further characterization employed the use of HR-ESI-MS and MALDI-TOF MS, which were able to provide unambiguous evidence of the absence of Lanthanum ions in the final complexes, as well as the distinct composition and purity of the desired products 1, 2 and 3 (Fig. S4-S9).

Finally, $^1$H NMR Spectra were employed for structural confirmation, particularly as regards the positioning of the crown-substituted ligand (H$_{Pc}^{in/out}$), and CH$_2$ protons from the crown-ether substituents themselves. The assignment of $^1$H-NMR spectra was made through the application of previously developed approaches for characterizing paramagnetic metal-containing trisphthalocyaninates; through the shifting of their resonance signals in comparison with that of their diamagnetic counterparts.37,38,39 Thus, through this method we were able to assign the shifts shown in Fig. 2, where the positioning of various signals is altered by the position of the corresponding diamagnetic and paramagnetic ions. This is due to the fact that the lanthanide-induced shift (LIS) phenomenon in NMR signals is dependent both on the nature and arrangement of the diamagnetic nuclei and paramagnetic lanthanide ion.

Magnetic Characterization

In order to probe our goal of inducing stronger 4f interactions through uniquely substituted heteroleptic ligands, we performed static magnetic susceptibility studies. Direct current (dc) magnetic measurements were performed on all samples between 1.8 and 300 K, with an applied dc field of 1000 Oe. The temperature dependence of the χ$^T$ product for all samples can be observed in Fig. 3.
master curve. These properties indicate the presence of non-negligible magnetic anisotropy and/or low-lying excited states.

Given that Tb\textsuperscript{III} sandwich complexes with Pc ligands have become some of the highest-performing Single-Molecule Magnets to date, we chose to investigate the magnetisation dynamics of 1-3 through ac susceptibility studies. Under zero applied static dc field and a small 3.78 Oe oscillating field there was a significant temperature dependent ac signal observed for 1. The dynamic behaviour was therefore investigated at various frequencies (0.1-1500 Hz) between 28 and 1.9 K. Frequency dependent in-phase ($\chi'$) and out-of-phase ($\chi''$) magnetic susceptibility data was fit using the corresponding generalized Debye models for a single relaxation process, with a distribution ($\alpha$) of relaxation times ($\tau$).\textsuperscript{45,46} The corresponding plots of fitted data can be observed in Fig. 4 and S13. The effective energy barrier and relaxation time were obtained through fitting the data using the Arrhenius equation ($\tau = \tau_0 \exp(U_\text{eff}/kT)$, which elicited a value of $U_\text{eff} = 229.9(0)$ K ($\tau_0 = 7.1(4)$x$10^{12}$ s), as can be seen in Fig. 5 and S13. This thermal relaxation barrier is attributed to the energy gap between ground and first excited Stark sublevels, and is consistent with previously reported barriers of 149 cm\textsuperscript{-1},\textsuperscript{31,43} and 230 cm\textsuperscript{-1} for homoeptically substituted Tb\textsubscript{III}Pc\textsubscript{3} complexes.\textsuperscript{31,43,47}

The speed of relaxation is related to both the $f$-$f$ interaction between Tb\textsuperscript{III} ions, and to the symmetry of the crystal field around the Tb\textsuperscript{III} ion. In the mononuclear Tb\textsubscript{III}Pc\textsubscript{3} molecule, the SAP $D_{4d}$ symmetry inherently has no mixing amongst $|J_f\rangle$ states due to the diagonal matrix elements.\textsuperscript{22,24} However, if that SAP symmetry is lowered, the introduction of off-diagonal matrix elements allows admixing of states, thus leading to faster relaxation processes. In this case we clearly observe a reduction in the SAP symmetry, as compared with previously reported Tb\textsuperscript{III} triple-decker phthalocyanine complexes discussed above, thus leading to a lower energetic barrier to magnetic relaxation. Interestingly, 1 does not display the same distinct relaxation processes for each Tb\textsuperscript{III} ion that was observed in the Tb/Tb version of the aforementioned systems.\textsuperscript{22,24} This could be due to a more closely related SAP coordination environment between Ln ions, or a stronger $f$-$f$ coupling interaction between Tb\textsuperscript{III} ions.

For 2 and 3 no significant temperature dependent signal was observed under zero applied dc field, however, under an applied dc field of 1000 Oe a signal was observed for both complexes. Such behaviour is indicative of faster relaxation processes, likely due to the aforementioned admixing of states in lower symmetry environments. In comparison to 1, these complexes do not have close dipolar contacts due to the diamagnetic Y\textsuperscript{III} ion, and therefore they cannot experience the same coupling interaction to aid in hindering the admixing of states. Thus, through the application of a static magnetic field we are able to lift the degeneracy of these states, and thus clearly observe the faster relaxation processes.

At room temperature the observed $\chi T$ values are as follows: 23.62 cm\textsuperscript{3}Kmol\textsuperscript{-1} (1), 11.81 cm\textsuperscript{3}Kmol\textsuperscript{-1} (2), and 11.79 cm\textsuperscript{3}Kmol\textsuperscript{-1} (3). The values are very consistent with the theoretical values of 11.82 cm\textsuperscript{3}Kmol\textsuperscript{-1} and 23.64 cm\textsuperscript{3}Kmol\textsuperscript{-1} for one and two non-interacting Tb\textsuperscript{III} ions ($F_{\text{II}}$, $S = 3$, $L = 3$, $g = 3/2$), respectively. The $\chi T$ product remains fairly stable upon decrease in temperature for all samples, until $\sim$30 K for 1; where a gradual increase can be observed prior to a more dramatic increase to 33.46 cm\textsuperscript{3}Kmol\textsuperscript{-1} at 1.8 K. This behaviour is indicative of low temperature ferromagnetic interactions between Tb\textsuperscript{III} ions. This ferromagnetic interaction between the magnetic dipoles of Tb\textsuperscript{III} ions in triple-decker Tb/Tb phthalocyanine complexes has been attributed to the stabilization and interaction between the ground, $J_z = \pm 6$, state spins.\textsuperscript{22,24,40-44} The low temperature behaviour for 2 and 3 is similar, displaying a plateau to values of 9.94 cm\textsuperscript{3}Kmol\textsuperscript{-1} and 9.22 cm\textsuperscript{3}Kmol\textsuperscript{-1}, respectively. The consistently observed slight negative deviation of the $\chi T$ product from 300 K is most likely attributed to a combination of possible factors, such as: inherent magnetic anisotropy present in Tb\textsuperscript{III} and/or depopulation of excited states. These results are consistent with previously studied triple-decker Tb/Y phthalocyanine complexes.\textsuperscript{22,24,40,42}

Confirmation of the presence of magnetic anisotropy was achieved through the collection of isotherm magnetisation data between 1.8 and 7 K (Fig. S10, S11, and S12). In each complex the $M$ vs. $H$ data below 7 K demonstrates a rapid increase in the magnetization at low magnetic fields. A shoulder develops below 1 T, followed by a gradual increase of $M$ at 1.8 K to reach near magnetic saturation: 7.90 $\mu_B$ (1), 4.38 $\mu_B$ (2), 4.23 $\mu_B$ (3) at 5 T. The $M$ vs. $H/T$ data also displays similar behaviour for all three complexes, where at high fields isotherm temperature lines do not completely overlay onto a single $\chi T$ vs. $T$ curve (Fig. S10, S11, and S12). In each sample the isotherm magnetisation data is consistent with the low temperature behaviour and the magnetic susceptibility data. For 1 this is highlighted by the absence of magnetic anisotropy in the $M$ vs. $H$ data above 7 K, with the $M$ vs. $H/T$ data displaying a single relaxation process at 1000 Oe and 5 T. However, a distinct relaxation process is observed for 2 and 3 at 1000 Oe and 5 T. This is attributed to the decrease in SAP symmetry, as compared with previously reported homoeptically substituted Tb\textsubscript{III}Pc\textsubscript{3} complexes.\textsuperscript{31,43,47}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig.3.png}
\caption{Temperature dependence of the $\chi T$ product at 1000 Oe for: 1 (violet), 2 (green), and 3 (blue) samples.}
\end{figure}
The dynamic behaviour for these complexes was investigated through ac susceptibility measurements at various frequencies (0.1-1500 Hz) between 25 and 1.9 K and under an optimized applied dc field of 1500 Oe (Fig. 4). Frequency dependent in-phase ($\chi'$) and out-of-phase ($\chi''$) magnetic susceptibility data was fit using the corresponding generalized Debye models for a single relaxation process, with a distribution ($\alpha$) of relaxation times ($\tau$), and can be observed in Fig. 4, as well as S15 (2) and S17 (3). Effective energy barriers and relaxation times were obtained by fitting data using the Arrhenius equation ($\tau = \tau_0 \exp(U_{\text{eff}}/kT)$), which elicited values of $U_{\text{eff}} = 129.8(0)$ K ($\tau_0 = 6.7(1) \times 10^{-7}$ s) for 2 (Fig. 5 and S14) and $U_{\text{eff}} = 168.1(8)$ K ($\tau_0 = 2.7(4) \times 10^{-7}$ s) for 3 (Fig. 5 and S16).

As was the case for 1, these results are relatively consistent with previously reported Tb/Y phthalocyanine triple decker complexes.$^{22,24}$ Since the previous Tb/Y studies did not report energetic barriers it is difficult to make a quantitative comparison. However, quantitatively, as discussed, SAP Tb$^{III}$ exhibits slower relaxation than SP Tb$^{III}$. Interestingly, another trend from the previous studies was that the SAP pocket with unsubstituted homoleptic Pc ligands exhibited slower relaxation than the heteroleptically substituted pocket.$^{24}$ In the case of 2 and 3 we observe similar field-induced behaviour was observed in both isolated Tb$^{III}$ systems, however, interestingly the heteroleptically substituted SAP Tb$^{III}$ displayed slower relaxation of the magnetization than the homoleptically substituted site. This was shown in the differing energy barriers for 2 and 3 under the same optimized applied dc field, which display the effect of the substituent-induced change in the coordination environment of the paramagnetic Tb$^{III}$ ion. The heteroleptically substituted coordination environment around the Tb$^{III}$ ion in 3 elicits a higher barrier to magnetic relaxation than the homoleptically substituted coordination environment of 2. This is likely due to the change in symmetry between the decks, as has been discussed above, as well as the electron donating substituents on the peripheral deck, where the paramagnetic metal ion in 3 is pushed closer to the outer Pc ligand, thus causing enhanced ligand field effects.$^{19}$ Cole-Cole plots ($\chi''$ vs. $\chi'$) for all complexes can be observed in Fig. 6, S15 and S17. These plots were employed in order to confirm the presence of single relaxation processes occurring within each complex. Furthermore, through fitting with a generalized Debye
model\textsuperscript{45,46} the extracted values for $\alpha$ and $\tau$ can be observed in Tables S1-S3.

Fig. 6 Cole-Cole plot for ac susceptibility data of 1 under 0 Oe applied dc field. Solid lines are the best fit to the generalized Debye model.

Conclusions
A detailed magnetic study of one homonuclear Tb\textsuperscript{III} and two novel heteronuclear Tb\textsuperscript{III}/Y\textsuperscript{III} phthalocyanine structures was performed. These complexes were synthesized in order to perform a magnetic study on a SAP Tb\textsubscript{2}Pc\textsubscript{3} complex with electron donating crown-ether substituents on two of the three ligands in the system. Thus, through isolating the paramagnetic ions separately in each pocket using diamagnetic Y\textsuperscript{III}, we were able to study Tb\textsuperscript{III} in a heteroleptic and homoleptic environment of electron donating substituents. We found that the $Jf$ coupling between lanthanide ions within a heteroleptic homonuclear crown-phthalocyanine complex was indeed of a non-negligible ferromagnetic nature. This magnetic dipolar interaction was able to lift the degeneracy of states, thus prohibiting the faster relaxation processes observed in the heterodinuclear complexes. Thus, a high energy barrier to magnetic relaxation was extracted. The two heterodinuclear complexes with Tb\textsuperscript{III} and Y\textsuperscript{III} displayed that the static behavior of the single paramagnetic ion was consistent between both structures, however, the dynamic measurements illustrated the significant effect of the altered environment, eliciting different energy barriers under the same optimized applied dc field. The complex with paramagnetic Tb\textsuperscript{III} in a heteroleptically substituted environment exhibited a higher energy barrier, likely due to increased symmetry in the square antiprismatic coordination environment, thus reducing faster relaxation processes due to admixing of states, as well as the presence of electron donating substituents on the central ring pushing the paramagnetic ion towards an enhanced ligand field from the unsubstituted Pc ligand. Thus, we can strive towards higher energy barriers in these complexes using the design principles of incorporating: $ff$ coupling, idealized SAP symmetry, and electron donating substituents on a heteroleptic Pc ligand. Through these design strategies, and others learned through fundamental studies such as these, we may design better magnetic materials.

Notes and references