Single-Molecule Magnets

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Coupling Dy_3 Triangles Enhances Their Slow Magnetic Relaxation**

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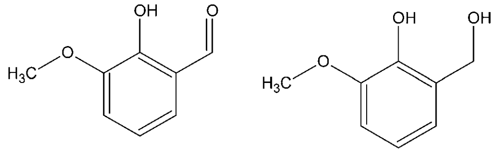
In memory of Philip Tregenna-Piggott

The discovery of single-molecule magnet (SMM) behavior, where relaxation and quantum tunneling of the magnetization is molecule-based due to the presence of a blocking anisotropy,[1] is recognized as an important breakthrough in the field of molecular-based magnetism. This has led to intense activity on the part of synthetic chemists to produce systems suitable for detailed study by physicists. A further aim is to produce and characterize new molecules with the goal of identifying features of relevance to enhancing or even discovering new properties compared with those of the originally studied examples. Recently, examples of molecules either incorporating[2] or made exclusively from 4f metal ions[3] have shown that lanthanide ions can produce fascinating magnetic behavior, not only through their potential to contribute high spins, but also to introduce anisotropy to a molecule as a result of the nature of the f-electron shell. Largely speaking, the magnetic behavior of such systems is difficult to explain in terms of simple spin models and therefore requires the development of new paradigms.

An example of such a paradigm shift is provided by the trinuclear dysprosium complexes we described in the compounds $[Dy_3(\mu_3\text{-}OH)_2L_3Cl_2(OH_2)_4][Dy_3(\mu_3\text{-}OH)_2L_3Cl(OH_2)_5]Cl_5\cdot 19H_2O$ (**1a**) and $[Dy_3(\mu_3\text{-}OH)_2L_3Cl(OH_2)_5]Cl_3\cdot 4H_2O\cdot 2MeOH\cdot 0.7MeCN$ (**1b**) (L = *o*-vanillato; Scheme 1).[3d] These Dy_3 triangles have an essentially diamagnetic ground state, which we were able to identify using single-crystal studies as the molecular archetype of the Ising non-collinear model.[4] These molecules display SMM behavior arising from an excited spin state, thereby giving a system with unprecedented magnetic properties. As part of our continuing studies on this type of trinuclear system,[3i] we have discovered a means of linking two such units to give a Dy_6 molecule with even more exotic magnetic properties.



Scheme 1. Structural formulae for *o*-vanillin, H**L**, (left) and 2-hydroxymethyl-6-methoxyphenol, H_2**L′** (right).

In the course of synthesizing analogous Ln_3 triangles for a systematic study of the system, which will be described elsewhere, and again using vanillin as ligand, it was found that for the thulium(III) compound, the hexanuclear complex, $[Tm_6(\mu_3\text{-}OH)_4L_4L'_2(H_2O)_{10}]Cl_6\cdot 18H_2O$ (**2**) formed. This formation results from the reduction of the aldehyde to an alcohol for one of the three *o*-vanillinato ligands on each triangle. The resulting alkoxides lead to a double bridge between two of the triangular Tm_3 motifs. With the interesting magnetic behavior of the Dy_3 triangle in mind, we directed the synthesis to the Dy_6 analogue by deliberately adding 2-hydroxymethyl-6-methoxyphenol, H_2L', to the reaction, leading to the formation of $[Dy_6(\mu_3\text{-}OH)_4L_4L'_2(H_2O)_9Cl]Cl_5\cdot 15H_2O$ (**3**) in good yields. Such metal-ion-catalyzed ligand transformations are now relatively frequently reported in the literature, and the most relevant example to this work is the dysprosium(III)-activated[3h] transformation involving acetone and *o*-vanillin.

Compounds **2** and **3** are isomorphous, crystallizing in the triclinic space group $P\bar{1}$ with $Z = 1$ (Supporting Information) but with 1:1 disorder of water and chloride on one terminal site in **3**. Herein we only discuss the structural features with reference to **3** further, as this is the compound displaying the most interesting magnetic behavior. The Dy_6 structure seen in **3** can be considered as resulting from the formal linkage by the alkoxides of the reduced form of the ligand of two of the Dy_3 triangles in **1** with the concomitant formal loss of the two terminal chloride ligands (Figure 1).

The triangular Dy_3 unit in **3** is less equilateral than found for **1**,[3d] with Dy···Dy distances of 3.5127(3), 3.5371(3), and 3.5797(3) Å. The inter-triangle Dy3 ···Dy3′ distance is 3.7262(4) Å. The planes of the two triangles in the Dy_6 unit are strictly co-parallel, but not coplanar, and the perpendicular distance between them is 2.4757(6) Å, with the Dy3···Dy3′ vector at 48.4° to the normal of the Dy_3 planes.

A DC magnetic susceptibility measurement of **3** showed a χT product at room temperature of 82.3 emu K mol^{-1}, as expected for six noninteracting f^9 ions, and a monotonic decrease upon lowering the temperature (Supporting Infor-

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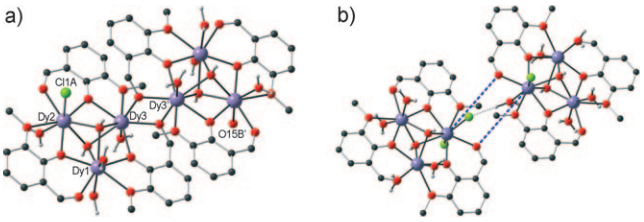

Figure 1. a) Structure of the $[Dy_6(\mu_3\text{-}OH)_4L_4L'_2Cl(H_2O)_9]^{5+}$ cation in **3** (Dy blue, Cl green, O red). For clarity, only the chloride, Cl1A, of the disordered Cl/H_2O is shown on Dy2 and only the water oxygen O15B′ on the inversion-related Dy2′. Non-water hydrogen atoms omitted for clarity. b) The formal formation of **3** by coupling two Dy_3 clusters in **1b**, by the loss of two terminal chloride ligands and formation of two Dy–O bonds (dotted blue lines) involving the alkoxides of the reduced ligand.

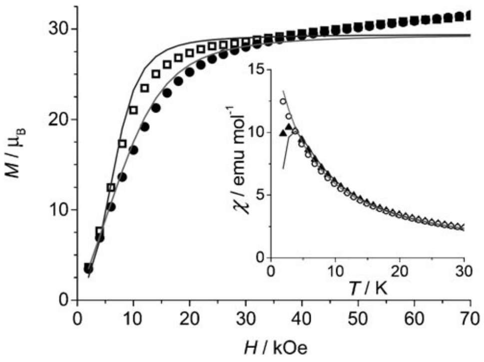

Figure 2. Field dependence of the molar magnetization measured on a pellet of polycrystalline powder of Dy_6 at $T = 1.8$ K (●) and $T = 4.0$ K (□). Inset: temperature dependence of the magnetic susceptibility on a polycrystalline powder at $H = 1$ kOe (▲) and $H = 10$ kOe (○). Lines correspond to the calculated values (see text) obtained from the simultaneous simulation of single-crystal data.

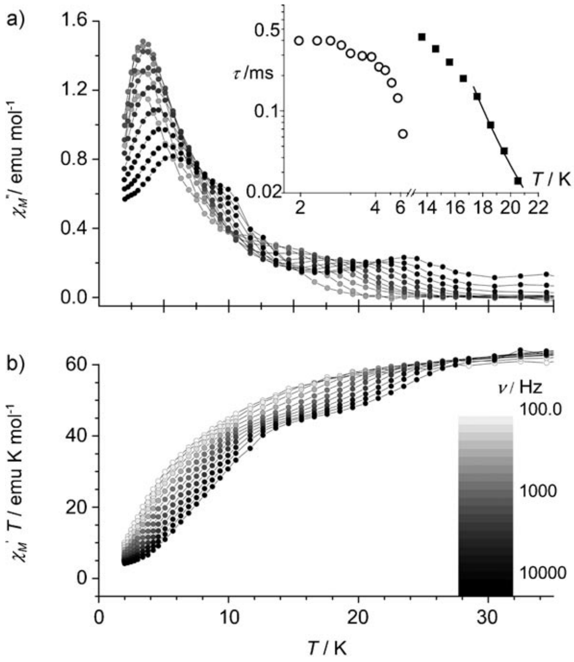

Figure 3. Temperature dependence of a) AC magnetic susceptibility for Dy_6 of imaginary component and b) $\chi' T$ product in zero static field. Inset: temperature dependence of the relaxation time for the low-temperature (■) and high-temperature processes (○) are shown; the high-temperature data is fitted using the Arrhenius law (——).

mation, Figure S2). The low-temperature behavior of the susceptibility is more informative (Figure 2, inset), in which a maximum around $T = 3$ K is observed with an external field of 1 kOe. In contrast, this maximum occurs at $T = 7$ K in **1**. A constant increase is observed with an applied field of 10 kOe. The application of a moderate field is able to overcome the weak antiferromagnetic (AF) interactions and to suppress the maximum in the susceptibility. The magnetization measured under variable field at 1.8 K shows an inflection around 0.5 kOe, see Figure 2, and reaches a plateau at about 30 kOe with a value of $28\mu_B$, corresponding to twice the value observed for **1**, with a similar weak linear increase at higher fields. The behavior is therefore broadly similar to that of the Dy_3 clusters in **1**[3d] but the antiferromagnetism is less pronounced, in spite of the fact that Dy_6 comprises an even number of interacting centers.

The dynamics of the magnetization were investigated using AC susceptibility measurements, with the results in zero static field given in Figure 3. Most striking is the presence of two regions in which the susceptibility shows a strong frequency dependence. The out-of-phase component χ'' shows a series of frequency-dependent peaks around 25 K, with a second set around 5 K. In contrast, Dy_3 showed a unique set of maxima around 8 K. The curves of $\chi' T$ versus T (Figure 3b) are more helpful in quantifying the relative fraction of magnetization involved in the two relaxation processes and suggest that the high-temperature slow relaxation process involves a significant fraction (about 25%) of the magnetization. The difference in the magnetization dynamics compared with Dy_3 is also clear from the field dependence of the AC susceptibility. The application of a field of 1 kOe has practically no effect on the dynamics (Supporting Information, Figure S3), while a dramatic slowing down was observed in the case of for Dy_3,[4] suggesting that the tunneling in zero field is less efficient in Dy_6 than in Dy_3.

To investigate this complex behavior further, the relaxation time τ was extracted from the isothermal frequency dependence of the out-of-phase component of the susceptibility, assuming that at its maximum $\tau = (2\pi\nu)^{-1}$. The results show a marked deviation from an Arrhenius law, with a leveling of τ on lowering the temperature more evident for the low-temperature process. The Arrhenius analysis for the higher temperature data gives $\Delta E = 200(10)$ K, $\tau_0 = 1.5(5) \times 10^{-9}$ s.

As the unique features of the parent compound Dy_3[3d,4] originated from the arrangement of the Dy^{3+} easy axes at 120° to each other in the triangular plane, giving the first molecular example of a system showing the classic non-collinear orientation of Ising spins seen in condensed phase materials, we decided to investigate the single-ion magnetic anisotropy in Dy_6 by performing complete active space (CASSCF) calculations for the three different Dy^{3+} ions, including the effect of the spin–orbit coupling[5] (Supporting Information). This high-level ab initio method was previously used to determine the single-ion easy anisotropy axes and gyromagnetic factors for the Dy^{3+} ions in Dy_3 and was in almost perfect agreement with the experimental results performed on single crystals.[6] The validity of the method was confirmed for two further Dy^{3+} compounds.[3i,7,8] The computed large anisotropy of the gyromagnetic factors ($g_z \gg g_x, g_y$) and the large energy gap between the ground and first excited Kramer's doublet justify the Ising approximation used. Also the g_z values of about 20 indicate an almost pure $|m_j = \pm 15/2>$ ground-state doublet.[9]

Figure 4 shows the computed single-ion easy anisotropy axes, where θ is the angle subtended by an easy axis with respect to the plane of the triangle and ϕ is the angle between the projection of each easy axis on to the plane of the triangle and the corresponding bisector of the triangle. The directions of the local easy axes for Dy1 and Dy2 in **3** lie almost in the plane of the triangle ($\theta < 3°$) and are tangential to the triangle with ϕ ranging between 82.1 and 82.4°. These results are essentially the same as those found for the Dy_3 system, consistent with the similar ligand environments of Dy1 and Dy2 in the two compounds. However, there is the important difference that the local easy axis for the central Dy3 ions deviates by about 10° out of the plane of the triangle and makes a smaller angle (64.2°) to the bisector, reflecting the rather different coordination environment resulting from the alkoxo bridges to the second triangle.

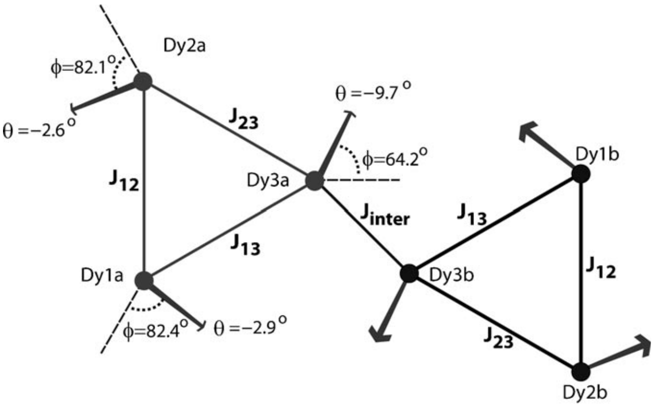

Figure 4. The calculated six easy axes. The arrows represent the positive directions of the associated local *z* axes used in the spin Hamiltonian [Eq. (1)] and the angles of these to the plane defined by the triangular moeity (θ). The angles of their projections on to the triangular plane with the bisector of the triangle (ϕ) are also indicated. Lighter lines indicate that the first triangle lies behind the second, whilst the shape of the arrows is indicative of their relative orientation with respect to the plane the page. The magnetic interactions derived from the spin Hamiltonian are also shown.

To evaluate the effects of the breaking of the trigonal symmetry characteristic of Dy_3, we decided to perform a single-crystal magnetic characterization. The triclinic space group is well suited for this kind of investigation, as only one orientation of the cluster is present in the crystals. However, three orthogonal rotations are necessary to define the susceptibility tensor satisfactorily. Unfortunately, the presence of solvent molecules of methanol and acetonitrile in the crystal lattice makes the crystal very unstable, precluding precise indexing of the crystal faces and correct orientation of the crystal on the sample rotator. We therefore developed a new method to deal with this by embedding the crystal in glue (or grease) on one face of a millimeter-sized Teflon cube, which can then be mounted on a goniometer head, thus enabling crystal indexing using an X-ray diffractometer. As Teflon is a polymer and does not diffract, the metric matrix is defined by the crystal alone. Three rotations along the **X**, **Y**, and **Z** orthogonal axes defined as the normal to three faces of the cube were performed. These faces can be indexed with non-integer Miller indices within the reference frame of the crystal (Supporting Information). This new procedure we have developed allows for much easier handling of crystals that are air-sensitive, susceptible to solvent loss, or with poor habit, and thus enables the results to be correlated accurately to the molecular structure.

This investigation showed, as expected, a large angular dependence of the magnetization (Supporting Information, Figure S4). In stark contrast to what was observed in Dy_3 and monomeric Dy systems, the positions of the maxima and minima change significantly on going from 1.9 K to 10 K, but remain almost unaltered up to the highest investigated temperature (25 K). To extract more precise information on this extraordinary behavior, the data were fitted assuming a tensorial relation $\mathbf{M} = \boldsymbol{\chi}\mathbf{H}$,[8,10] which for each rotation reduces to:

$$M(\theta) = \chi_{\alpha\alpha} H(\cos\theta)^2 + \chi_{\beta\beta} H(\sin\theta)^2 + 2\chi_{\alpha\beta} H \sin\theta\cos\theta \qquad (1)$$

where α and β correspond to the versors (unit vectors) of **X**, **Y**, and **Z** in a cyclic permutation and θ is the angle between **H** and the $\boldsymbol{\alpha}$ versor.

The susceptibility tensors $\boldsymbol{\chi}$ can be diagonalized, and are presented pictorially in Figure 5 for $T = 2.0$ K and $T = 10$ K as ellipsoids superimposed on to the molecular structure of the cluster. The principal values are summarized in the Support-

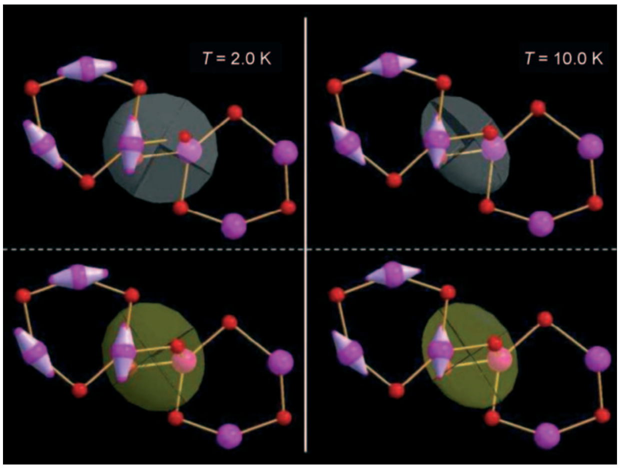

Figure 5. Ellipsoidal representation of the experimental (top) and calculated (bottom) susceptibility tensors of Dy_6 at two different temperatures. The tensors are superimposed onto the molecular structure of the magnetic core (Dy violet, O red); the orientation of the Dy easy axes estimated from ab-initio calculations are also shown.

ing Information, Table S2. It is clear that while at 2.0 K the magnetic anisotropy is of the easy-plane type and essentially isotropic within the plane, on increasing the temperature this assumes an Ising (easy axis) character.

This behavior is unprecedented and can be attributed to the way in which the two triangles have been linked. To explore this further, the angle-resolved single-crystal magnetic data of compound **3** were fitted with an Ising spin Hamiltonian by considering each Dy^{3+} as an Ising spin with $S=1/2$, as we previously did for Dy_3:[3d,4]

$$H = -J^{z}_{\mathrm{int}} S^{3a}_{z_3} S^{3b}_{z_3} - \sum_{\substack{i,j=1,2,3 \\ i<j}}^{n=a,b} J^{zz}_{ij} S^{in}_{z_i} S^{in}_{z_j} - \sum_{i=1,2,3}^{n=a,b} g_{z_i} S^{in}_{z_i} H_{z_i} \tag{2}$$

where the index n refers to the two different triangular moieties, denoted as a and b, and the indexes i and j refer to the three different Dy^{3+} ions in each triangle (Figure 4). $S^{in}_{z_i}$ denotes the spin operator for the *in*th Dy^{3+} (Dy3) along its local easy anisotropy axis z_i. J^{zz}_{ij} corresponds to the Ising magnetic interactions within the triangular moiety and J^{z}_{int} the magnetic interaction between the two Dy3 ions in different triangles. Finally, g_{z_i} and H_{z_i} are the gyromagnetic factors and the applied magnetic field, respectively, along the z_i local axes. The fact that the two triangular moieties are related by an inversion center is taken into account, and therefore the local axes z_i and the parameters J^{z}_{ij} and g_{z_i} do not depend on the triangle index n. Using the g_{z_i} gyromagnetic factors ($g_{z_1}=19.8$, $g_{z_2}=19.7$, $g_{z_3}=19.3$) and the directions of the z_i local axes previously obtained from the ab initio calculations, the unknown parameters of the Hamiltonian model are the four independent magnetic interactions indicated in Figure 4. The simulation of the angle-resolved magnetic susceptibility data gives $J^{zz}_{12}=7.6$ K, $J^{zz}_{13}=6.0$ K, $J^{zz}_{23}=5.0$ K, and $J^{z}_{\mathrm{int}}=1.2$ K. It should be noted that the positive signs correspond to antiferromagnetic interactions, because in our spin Hamiltonian the local z axis vectors defined in Figure 4 of two interacting Dy^{3+} ions subtend an angle larger than 90°.

The complete simulation of all the rotations is shown in the Supporting Information, Figure S4 and the calculated powder data in Figure 2. Only a partial agreement is expected at this level of approximation, as all transverse components of the dysprosium ions have been neglected in our models and the easy axes directions have been fixed to those resulting from the ab initio calculation. The out-of-plane components are therefore significantly smaller in the calculated tensors but the trend in the change of the magnetic anisotropy is however reproduced as shown in Figure 5 where the calculated susceptibility tensors are also indicated.

The calculated energies as a function of the magnetic field applied in the plane (Supporting Information, Figure S6) show that the ground state of Dy_6 is a non-magnetic doublet as in the case of Dy_3.[6] This results from the weak AF interaction between the triangles. However, due to the breaking of the trigonal symmetry and a larger deviation of the easy axis of Dy3 from the plane of the triangle, a weakly magnetic state is found at only 0.6 K above the ground state (compared with about 10 K in Dy_3). The disappearance of a step in the M versus H curve is therefore not surprising. The first excited state corresponds to the violation of J_{inter}, this being the weakest interaction, and does not affect the clockwise or anticlockwise arrangement of the magnetic moments in each triangle.

We can try to rationalize the dynamics of the magnetization of Dy_6 in the frame of the model we have developed. The main feature of Dy_6 is the presence of two different relaxation processes, one with rates comparable to those found for Dy_3, and a second one with much higher blocking temperatures. It would be tempting to associate the high-temperature slow relaxation to the Dy3 site, which has a different coordination environment compared with the original Dy_3 molecule, but this disagrees with the finding that this site has a smaller calculated energy gap between the ground and the first excited doublet (Supporting Information, Table S3). Moreover, similar differences in the energy gaps were also calculated for Dy_3 but not observed in the dynamic behavior. An alternative explanation could be that it arises from the peculiar change in magnetic anisotropy from easy plane to easy axis on populating the excited states. It is intuitive that the more anisotropic character of the excited states can result in a slower relaxation process observed at higher temperature when these states have strong contributions to the AC susceptibility. The absence of faster relaxation in zero static field, which on the contrary was clearly evident in Dy_3, can also be associated to the linking of the two triangles. Relaxation through quantum tunneling is strongly suppressed when it involves simultaneous magnetic flipping of more than one site, as has already been observed in weakly coupled dimers of Mn_4 SMM.[11]

In conclusion, the linking of two Dy_3 to form Dy_6 has been found to give a spectacular increase in the temperature at which slowing down of the magnetization is observed from 8 to 25 K. This occurs in spite of the fact that the linking promotes an antiferromagnetic interaction, in contrast to what was recently observed for a similar arrangement of Dy_3 triangles,[3h] where a ferromagnetic interaction was suggested. The observation of two relaxation regimes is apparently associated to an unprecedented change in the nature of the magnetic anisotropy from an easy plane to easy axis type on increasing the temperature. This change can be explained by breaking of the symmetry induced by linking the triangles. We can further note that this behavior contrasts to what is normally encountered in anisotropic systems on reducing temperature, where they are expected to become more, rather than less, anisotropic at low temperature. Although this needs verification with reference to other systems, it is a very exciting finding that a relatively long relaxation time, useful for instance in molecular spintronics devices, can be observed at high temperatures thanks to the properties of the excited states. More information on the temperature dependence of the magnetic anisotropy of complex molecules containing lanthanide ions is needed, in particular from oriented single crystal studies, in order to establish magnetostructural correlations. Fortunately, the straightforward single-crystal sample handling procedure developed herein can easily be applied to angle-resolved magnetometry on a wide range of compounds and should lead to the desired insights being gained rapidly.

Experimental Section

For synthetic details, see the Supporting Information.

Magnetic characterizations were carried on fresh crystals crushed and pressed in a pellet to avoid orientation in the magnetic field. DC measurements were performed with a Quantum Design SQUID magnetometer, whereas for AC investigations a home-built inductive probe was used in conjunction with an Oxford Instruments MAGLAB2000 platform. Angle-resolved magnetic measurements were performed with an horizontal sample rotator adapted to a Cryogenic S700 Squid magnetometer. CASSCF/RASSI-SO calculations employed MOLCAS-7.0.[12] For further details, see the Supporting Information.

X-ray crystallographic data for **2**: $C_{48}H_{104}Cl_6O_{50}Tm_6$, 2707.59 $\mathrm{g\,mol^{-1}}$, triclinic, $P\bar{1}$, $a = 11.8833(10)$, $b = 13.7484(13)$, $c = 14.0584(13)$ Å, $\alpha = 98.334(7)$, $\beta = 113.349(7)$, $\gamma = 90.894(7)°$; $U = 2079.7(3)$ Å^3, $Z = 1$, $T = 150$ K, $F(000) = 1308$, $\rho_{\mathrm{cald}} = 2.162\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 6.662\ \mathrm{mm^{-1}}$; 13874 data measured, 8220 unique ($R_{\mathrm{int}} = 0.0214$), 536 parameters, $wR_2 = 0.1217$, $S = 0.994$ (all data), $R_1 = 0.0452$ (6663 with $I > 2\sigma(I)$).

3: $C_{48}H_{96}Cl_6O_{46}Dy_6$, 2596.95 $\mathrm{g\,mol^{-1}}$, triclinic, $P\bar{1}$, $a = 11.9712(6)$, $b = 13.7566(7)$, $c = 14.0133(7)$ Å, $\alpha = 97.935(1)$, $\beta = 113.718(1)$, $\gamma = 90.368(1)°$; $U = 2087.71(18)$ Å^3, $Z = 1$, $T = 100$ K, $F(000) = 1250$, $\rho_{\mathrm{cald}} = 2.066\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 5.584\ \mathrm{mm^{-1}}$; 10665 data measured, 8978 unique ($R_{\mathrm{int}} = 0.0143$), 578 parameters, $wR_2 = 0.0881$, $S = 1.033$ (all data), $R_1 = 0.0320$ (8077 with $I > 2\sigma(I)$).

CCDC 724166 **2** and CCDC 724167 **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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