







according to the experimental data. The best agreement is found for  $J^{ex} = -0.79 \text{ cm}^{-1}$  leading to the exchange spectrum in Table S8. The computed dc magnetic properties are represented in Fig. 2. Superexchange interactions through bromide bridges override dipolar coupling because of the orthogonality between the easy magnetic axes, a spectacular effect of the peculiar *cis/trans* topology in the dimer.

The calculated transition magnetic moment elements, obtained from the *ab initio* single-ion analysis, are depicted in Fig. 5. Let us mention that this interpretation does not directly take into account hyperfine interactions<sup>16</sup> and spin-phonon couplings.<sup>17</sup> For Dy1, the ground and first excited state QTM components are found to be negligible ( $0\text{-}10^{-2} \mu_B$ ) and a significant magnetic axiality is still maintained in the 2<sup>nd</sup> excited state. Therefore, the most probable relaxation pathway involves the third excited state with an energy barrier of approx.  $600 \text{ cm}^{-1}$ , slightly higher than the experimental data (about  $500 \text{ cm}^{-1}$ ). On the contrary, a faster relaxation pathway is predicted for Dy2. The calculated transverse transition matrix element between the ground state KD is already large ( $0.14 \mu_B$ ), promoting a faster QTM compared to Dy1. While experimentally we cannot discriminate the two Dy<sup>III</sup> sites (one single relaxation), the calculations evidence the presence of two drastically different magnetic centres: i) a strongly anisotropic one (Dy1) with the two *trans* Cy<sub>3</sub>PO ligands; ii) Dy2, with the LF dictated by the *cis* configuration of the Cy<sub>3</sub>PO ligands, inducing a lower magnetic anisotropy character and a faster relaxation mechanism.

In summary, the first bromine-bridged octahedral dinuclear Dy<sup>III</sup> SMM has been synthesized and characterized. The complex presents a stereoisomeric dimer system with drastically different local anisotropies. Superexchange interactions through bromide bridges override dipolar coupling because of the orthogonality between the easy magnetic axes. Calculations suggest that the observed magnetic relaxation is dominated by the strong axial anisotropy of one dysprosium centre. The second dysprosium ion, with an almost planar anisotropy, is monitored through superexchange interaction. Polymetallic lanthanide systems based on asymmetric building blocks with perpendicular anisotropy arrangements still offer a playground for investigation of relaxation mechanisms in lanthanide SMMs.

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## Conflicts of interest

There are no conflicts to declare.

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