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# Synthesis, structure and magnetic properties of the dinuclear complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Dy_2$ coordinated by *ansa*-bis(amidinate) ligands with a *m*-phenylene linker

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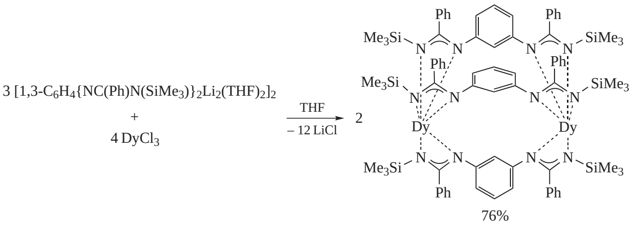
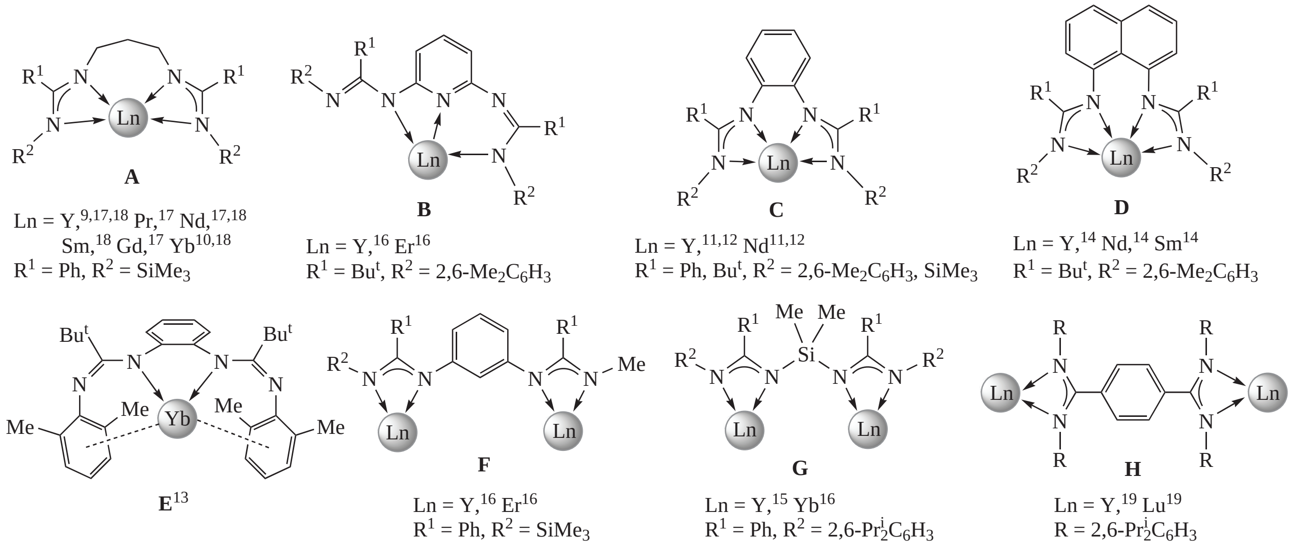
**A salt metathesis reaction of anhydrous $DyCl_3$ and $[1,3\text{-}C_6H_4\text{-}\{NC(Ph)N(SiMe_3)\}_2Li_2(THF)_2]$ in THF affords the complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Dy_2$ regardless of a ratio between reagents. The assembling of a binuclear core results from a spanning coordination of the amidinate fragments of three μ-bridging *ansa*-bis(amidinate) ligands to two $Dy^{3+}$ ions. The magnetic properties of the product were studied by SQUID magnetometry in a temperature range of 1.8–300 K.**



New molecular architectures with interesting physical characteristics, in particular, the properties of single ion (SIM) or single molecular (SMM) magnets,[1] can be prepared using the methods of organolanthanide chemistry and can serve as promising materials for creating devices for data storage and processing.[2] Paramagnetic lanthanide ions, which are characterized by large magnetic moments in combination with strong magnetic anisotropy, are of particular interest for the design of monomolecular magnets.[3,4] In addition, the control of the geometry of the coordination environment of a lanthanide ion is also a determining factor in the creation of mononuclear SMMs.[5,6] The coordination chemistry of lanthanide ions, mainly governed by their size and polarizability, led to complexes with high coordination numbers, in which the symmetry and coordination geometry are dictated only by ligands.[7,8] For these reasons, the steric factors, charges and donor strengths of the ligands play an important role in the design of SIMs. Dianionic linked bis(amidinate) ligands are of special interest as they enable the design of new architectures.[9–19] Specifically, depending on a number of factors (the length, nature, structure and conformational rigidity of the group binding two amidinate fragments), mono- or dinuclear structures can be assembled (Figure 1).

Here, we report the synthesis and structure of complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Dy_2$ **2** from the *ansa*-bis(amidinate)



**A**
$Ln = Y$,[9,17,18] Pr,[17] Nd,[17,18] Sm,[18] Gd,[17] Yb[10,18]
$R^1 = Ph$, $R^2 = SiMe_3$

**B**
$Ln = Y$,[16] Er[16]
$R^1 = Bu^t$, $R^2 = 2,6\text{-}Me_2C_6H_3$

**C**
$Ln = Y$,[11,12] Nd[11,12]
$R^1 = Ph, Bu^t$, $R^2 = 2,6\text{-}Me_2C_6H_3, SiMe_3$

**D**
$Ln = Y$,[14] Nd,[14] Sm[14]
$R^1 = Bu^t$, $R^2 = 2,6\text{-}Me_2C_6H_3$

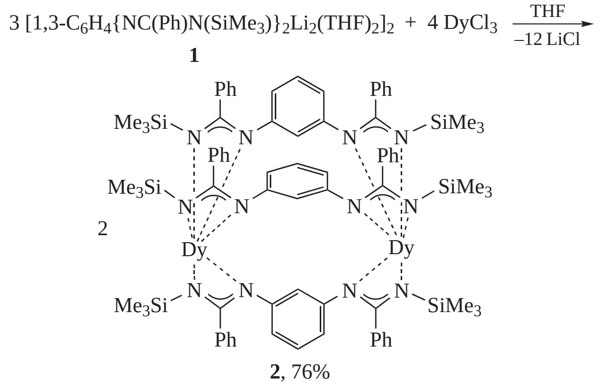
**E**[13]

**F**
$Ln = Y$,[16] Er[16]
$R^1 = Ph$, $R^2 = SiMe_3$

**G**
$Ln = Y$,[15] Yb[16]
$R^1 = Ph$, $R^2 = 2,6\text{-}Pr^i_2C_6H_3$

**H**
$Ln = Y$,[19] Lu[19]
$R = 2,6\text{-}Pr^i_2C_6H_3$

**Figure 1** Coordination modes of *ansa*-bis(amidinate) ligands containing different linkers to rare earth metal ions.



**Scheme 1**

ligand [1,3-$C_6H_4${NC(Ph)N($SiMe_3$)}$_2$$Li_2$(THF)$_2$]$_2$ **1** and $DyCl_3$ (Scheme 1). The magnetic properties of compound **2** were investigated using superconducting quantum interference device (SQUID) magnetometry in a wide temperature interval.

The synthesis of ligand **1** was described previously.[11] Its salt-metathesis reaction with anhydrous $DyCl_3$ in a molar ratio of 1 : 2 was performed in THF (25 °C, 48 h). Surprisingly, regardless of the molar ratio between the reagents, the reaction afforded the tris(amidinate) complex **2**, which was isolated as moisture- and air-sensitive colorless crystals in a 41% yield. When the reaction of **1** with $DyCl_3$ was performed with a molar ratio of 3 : 4, the yield of the product increased to 76% (see Scheme 1).

The X-ray diffraction study revealed that the molecule of complex **2** adopts a binuclear structure due to 'spanning' coordination mode of amidinate fragments of three μ-bridging *ansa*-bis(amidinate) ligands to two $Dy^{3+}$ ions (Figure 2).[†] Despite the similar ionic radii of $Y^{3+}$ (0.960 Å), $Er^{3+}$ (0.945 Å) and $Dy^{3+}$ (0.970 Å)[20] and similar isolation procedures, unlike [1,3-$C_6H_4${NC(Ph)N($SiMe_3$)}$_2$]$_3$Y(THF)Y(μ-Cl)Li(THF)$_3$ and [1,3-$C_6H_4${NC(Ph)N($SiMe_3$)}$_2$]$_3$$Er_2$(μ-Cl)Li(THF)$_3$, complex **2** crystallizes without LiCl(THF)$_3$ and coordinated THF molecules.

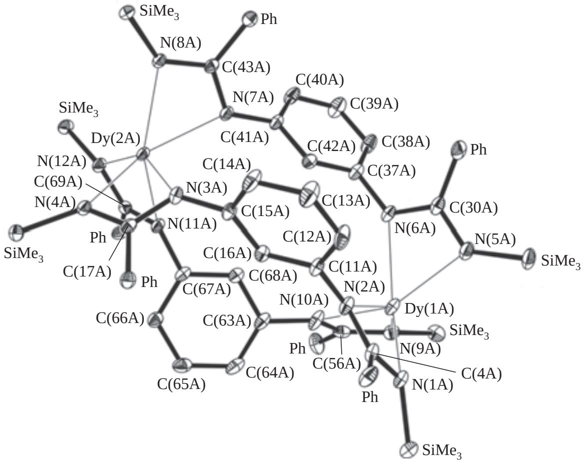


**Figure 2** Molecular structure of complex **2**. Thermal ellipsoids are given with a 30% probability.

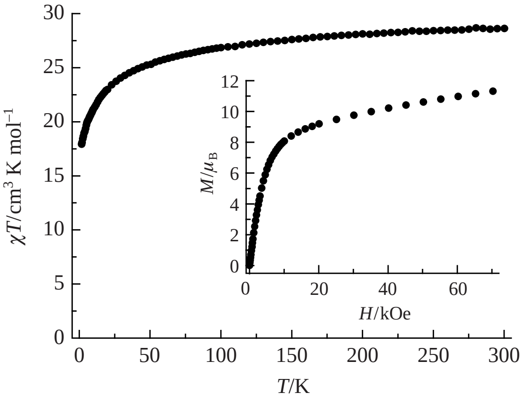


**Figure 3** Temperature dependence of $\chi T$ under a 1000 Oe dc field for **2**. Inset: field dependence of the magnetization at 1.8 K.

In its molecule, each $Dy^{3+}$ ion is coordinated by six nitrogen atoms of three amidinate fragments. Thus, the dysprosium cations have coordination numbers of 6 and the coordination environments of distorted trigonal prisms.

The magnetic properties of complex **2** were investigated using SQUID magnetometry in direct current (dc) and alternate current (ac) modes in a temperature range of 1.8–300 K and up to a magnetic field of 70 kOe. The experimental room temperature $\chi T$ value of 28.61 cm$^3$ K mol$^{-1}$ (Figure 3) is consistent with an expected value of 28.34 cm$^3$ K mol$^{-1}$ for two non-interacting $Dy^{3+}$ ions ($J$ = 15/2, $g$ = 4/3). A negative deviation of $\chi T$ is observed upon cooling to reach a value of 17.90 cm$^3$ K mol$^{-1}$ at 1.8 K. Such a behavior originates from the thermal depopulation of the $m_J$ sublevels. Since the $Dy^{3+}$–$Dy^{3+}$ intermetallic distance is long (7.330 or 7.346 Å), magnetic interactions between the spin carriers should be weak. The field dependence of the magnetization at 1.8 K reaches a value of 11.30$\mu_B$ under a 70 kOe dc field without a sign of saturation.

Taking into consideration a very high magnetic anisotropy of the $Dy^{3+}$ ion, we performed ac susceptibility measurements in order to probe the occurrence of slow magnetization relaxation associated with a single-molecule magnet (SMM) behavior, as recently demonstrated in organometallic $Dy^{3+}$ complexes.[21–30] Under a zero dc field, only weak frequency dependent out-of-phase signals could be detected (Figure 3), which could be ascribed to the strong quantum tunneling of magnetization (QTM). The absence of a maximum of $\chi''$ from the available temperature range precludes an in-depth analysis of the relaxation dynamics. Applying dc fields in the aim to shortcut the QTM did not lead to significant improvements. Clearly, the coordination environment in **2** appears not suitable to maximize the anisotropy and to induce a genuine SMM behavior. This fact can be rationalized based on electrostatic considerations.[6] Hence the three ligands arranged in a three branches star fashion around the $Dy^{3+}$ ions do not generate an axial crystal-field suitable to stabilize the oblate 4*f* electronic density and increase the anisotropy (Figure 4).

In conclusion, the dysprosium complex [1,3-$C_6H_4${NC(Ph)-N($SiMe_3$)}$_2$]$_3$$Dy_2$ was synthesized and structurally characterized. The geometry of *o*-phenylene linked bis(amidinate) ligand

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[†] *Crystal data for* **2**: $C_{78}H_{96}Dy_2N_{12}Si_6 \cdot 0.375\,C_6H_{14} \cdot 0.625\,C_4H_8O$, $M$ = = 1772.58, triclinic, $P\bar{1}$, $a$ = 14.8591(4), $b$ = 18.9190(5) and $c$ = 32.7637(8) Å, $\alpha$ = 86.2620(10)°, $\beta$ = 85.8900(10)°, $\gamma$ = 78.5590(10)°, $V$ = 8992.0(4) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.309 g cm$^{-3}$, $\mu$ = 1.776 mm$^{-1}$, a total of 90669 ($\theta$ = 26.04°) reflections, 35441 unique ($R_{int}$ = 0.0258), 2069 parameters, 583 restraints, $S$ = 1.046, $R_1$ = 0.0392 [$I > 2\sigma(I)$], $wR_2$ = 0.0935 (all data), largest difference peak/hole 2.99/–2.89 eÅ$^{-3}$.

The X-ray data were collected on a Bruker D8 Quest diffractometer [MoKα radiation, $\omega$-scans technique, $\lambda$ = 0.71073 Å, $T$ = 100(2) K] using the APEX3[31] software packages. The structures were solved by direct and dual-space methods and refined by full-matrix least squares on $F^2$ for all data using SHELX.[32,33] SADABS[34] was used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and refined anisotropically. Hydrogen atoms were placed in calculated positions and refined in the 'riding' model with $U(H)_{iso}$ = 1.2$U_{eq}$ of their parent atoms [$U(H)_{iso}$ = = 1.5$U_{eq}$ for methyl groups].

CCDC 1589142 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

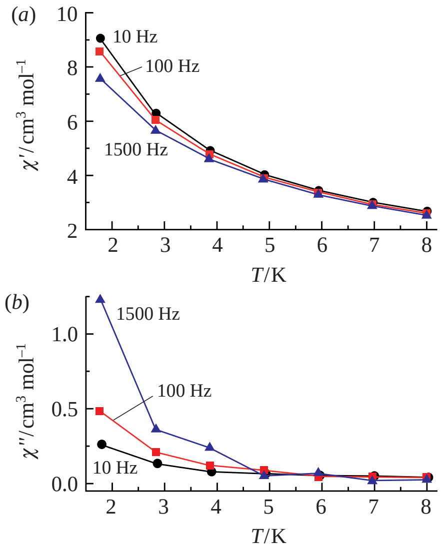

**Figure 4** Temperature dependence of the (*a*) in-phase ($\chi'$) and (*b*) out-of-phase ($\chi''$) susceptibilities under a zero dc field for **2**.

$[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_2^-$ proved to be favorable for assembling a binuclear core. The studies of magnetic properties of the complex in a temperature range of 1.8–300 K revealed the absence of $Dy^{3+}$–$Dy^{3+}$ interaction and SMM behavior in it.

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### *Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.024.

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