New π -Carbazolyl Dy(III) Half-Sandwich Complex Showing a Single-Molecule-Magnet Behavior

Jérôme Long, Alexander Selikhov, Konstantin A. Lyssenko, Yannick Guari, Joulia Larionova, Alexander A. Trifonov

► To cite this version:

Jérôme Long, Alexander Selikhov, Konstantin A. Lyssenko, Yannick Guari, Joulia Larionova, et al.. New π -Carbazolyl Dy(III) Half-Sandwich Complex Showing a Single-Molecule-Magnet Behavior. *Organometallics*, 2020, 39 (15), pp.2785-2790. 10.1021/acs.organomet.0c00426 . hal-02919788

HAL Id: hal-02919788

<https://hal.science/hal-02919788>

Submitted on 27 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

New π -carbazolyl Dy(III) half-sandwich complex showing a Single Molecule Magnet behavior.

Jérôme Long*,^a Alexander N. Selikhov,^{b,c} Konstantin A. Lyssenko,^{c,d} Yannick Guari,^a Joulia Larionova,^a Alexander A. Trifonov*^{b,c}

^a ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France.

^b Institute of Organometallic Chemistry of Russian Academy of Sciences, 49 Tropinina str., GSP-445, 603950, Nizhny Novgorod (Russia).

^c Institute of Organoelement Compounds of Russian Academy of Sciences, 28 Vavilova str., 119334, Moscow (Russia).

^d M.V. Lomonosov Moscow State University, Chemistry Department, Moscow, Russia 119991

ABSTRACT: We report the synthesis, structure and magnetic investigations of a new Dy³⁺ heteroleptic complex [Dy(*t*Bu₄Carb)(*o*-Me₂N-C₆H₄CH₂)₂] $\cdot$ C₇H₈ (**1**) (*t*Bu₄Carb = 1,3,6,8-Tetra-*tert*-butyl-9H-carbazole, *o*-Me₂N-C₆H₄CH₂)₂ = *o*-N,N-dimethylaminobenzyl). The carbazolyl ligand exhibits an unprecedented η^5 π -interaction with the magnetically anisotropic dysprosium(III) ion resulting in a genuine zero-field single-molecule magnet behavior.

Lanthanide coordination complexes have recently emerged in materials science owing to their intriguing Single-Molecule Magnet (SMM) behavior which opens exciting potentialities in information storage or spin-based computing.¹ Some lanthanides complexes are indeed able to exhibit a slow relaxation of their magnetization associated with a magnetic bistability at the molecular scale below a blocking temperature.² This phenomenon originates from the electronic structure of a specific lanthanide ion in a particular crystal-field that allows the appearance of an anisotropic barrier opposing two antiparallel directions of magnetic moment related to the $\pm m_J$ states.³

Among the lanthanide series, the Dy³⁺ Kramers ion exhibiting an oblate 4f electronic density, unambiguously gives the best SMM performances. Hence, following theoretical modeling predictions^{3a, 4} in association with electrostatic considerations,⁵ major advances have been achieved recently by engineering a high axial crystal-field for Dy³⁺ through designing mononuclear complexes with two negatively charged ligands along the axial direction with short bond lengths and weak coordinated species in the equatorial plane. Although coordination chemistry ligands have been used in this purpose,⁶ organometallic ligands such as cyclopentadienyl (Cp) derivatives gave exceptional magnetic features in dysprosium metallocene complexes⁷ with magnetic hysteresis that could even reach 80 K.⁸ Nevertheless, the use of other carbon-based organometallic ligands, such as cyclooctatetraene (COT) or systems with greater hapticity could hardly compete with the Cp derivatives in terms of SMM's performance. This could be ascribed to their increased hapticity which provides a larger binding site, more suitable to provide an equatorial field.⁹ As a consequence, the employment of rigid η^5 -ligands constitutes the most

appealing strategy to design high blocking temperatures SMMs. In particular, several studies lead to the improvement of SMM performances by substituting some Cp positions to increase the hysteresis temperature,^{7b, 8} or by introducing a heteroatom in the Cp backbone to shortcut the molecular vibration and provide larger crystal-fields.¹⁰ Thus, other η^5 -organometallic ligands, such as monophosphonyl¹¹ or dicarbollide ligands¹² were used. However, the SMM hallmarks were found less outstanding in comparison with authentic dysprosium metallocene complexes due to the difficulty to achieve a linear angle or the generation of on-resonance vibrational modes. The magnetic relaxation being extremely sensitive to subtle effects, new examples of original η^5 -ligands are therefore highly needed to understand the parameters affecting the relaxation and draw a general picture.

With this in mind, carbazole-based ligands constitute a tempting alternative to Cp derivatives. Indeed, these heterocyclic ligands exhibit a diversity in their coordination modes since they could act either as monoanionic σ -donor amido ligand but are also able to form π -complexes involving the five-membered pyrrole ring, while benefiting from a strong rigid character arising from multiple aromatic rings.¹³ They also show a great tunability in terms of substituent allowing to tune their steric hindrance and electronic features. Moreover, introducing novel functionalities, such as luminescence could be achieved since the rigid plane biphenyl core with wide band gap and high luminescent efficiency presents great opportunities for the synthesis of new emitters,¹⁴ and in turn for the design of luminescent SMMs.¹⁵

In this sense, while most of the carbazolyl complexes involves divalent lanthanide ions,¹⁶ we have recently reported that simple carbazolyl with a σ -donor interaction could be used to design Dy(III) SMMs.¹⁷ However, examples of π -carbazolyl complexes remain scarce and are strictly limited to divalent lanthanide ions.¹⁸ We would like also to emphasize that examples of Dy complexes with Dy/carbanion interactions are also limited.¹⁹

We report in this communication the synthesis, structure and magnetic investigations of a half-sandwich heteroleptic dysprosium complex showing an unprecedented η^5 -coordination mode of the carbazolyl ligand resulting in the appearance of an axial-crystal field and a zero-field SMM behavior.

Scheme 1: Synthesis of **1**.

The alkane elimination reaction of equimolar amounts of tBu_4CarbH and $[Dy(o-Me_2N-C_6H_4CH_2)_3]$ in toluene at $80^\circ C$ (25 min.) affords the heteroleptic complex $[Dy(tBu_4Carb)(o-Me_2N-C_6H_4CH_2)_2] \cdot C_7H_8$ (**1**) (Scheme 1) in 82% yield after recrystallization from hot hexane. Single crystals of **1** suitable for X-Ray analysis were obtained by slow concentration of the mother liquor at room temperature. Complex **1** is a bright yellow crystalline solid, oxygen- and moisture-sensitive. It is readily soluble in THF, Et_2O and aromatic solvents, sparingly soluble in hexane.

Analysis by single-crystal X-ray diffraction indicates that **1** crystallizes in the monoclinic $P2_1/c$ space group, with a unique complex in the asymmetric unit and a toluene solvate (Table S1). The compound could be described as a heteroleptic half-sandwich complex. The coordination environment of the Dy^{3+} ion consists in a η^5 -coordinated carbazoyl ligand, as well as two nitrogens and two negatively charged carbons from two bidentate $o-Me_2N-C_6H_4CH_2$ ligands (Figure 1a). In contrast to our recently reported dysprosium complexes based on an unsubstituted carbazole acting as a simple amido ligand,¹⁷ the introduction of bulky tertbutyl groups forces the π -coordination mode of the (tBu_4Carb) ligand. Hence, the $Dy-(tBu_4Carb)_{cent.}$ bond length is equal to $2.418(2)$ Å, which appears greater in comparison to the distances found in dysprosium metallocene with cyclopentadienyl derivatives.^{7-8, 20} For comparison, the $Dy-Cp^*$ and $Dy-Cp^{*Pr5}$ distances are equal to $2.296(1)$ and $2.284(1)$ Å, respectively, in the complex $[Dy(Cp^{*Pr5})(Cp^*)]^+$.⁸ In **1**, the $Dy-C$ distances involving $o-Me_2N-C_6H_4CH_2$ are comparable to the $Dy-(tBu_4Carb)_{cent.}$ one with values of $2.414(4)$ and $2.423(4)$ Å, while the $Dy-N$ bond lengths are significantly longer ($2.596(4)$ and $2.607(4)$ Å). It is especially worth noting the difference in the coordination type of the tBu_4Carb ligand with Dy^{3+} and Ln^{2+} .^{18a} In $[Ln(tBu_4Carb)_2]$ complexes ($Ln = Sm, Eu, Yb, Ca$), the coordination of carbazoyl ligands to Ln^{2+} ions features a strong contribution of η^3 -mode into η^5 metal-ligand bonding giving a displacement of the Ln^{2+} ion with respect to the centroid of the five-membered ring. In contrast for **1**, typical η^5 coordination mode occurred with a symmetric localization of the Dy^{3+} ion above the centroid of the pyrrolyl ring (Figure 1b). The $C35-Dy-C44$ angle strongly deviates from linearity with a value of $138.5(1)^\circ$ while the $C44-Dy-(tBu_4Carb)_{cent.}$ and $C35-Dy-(tBu_4Carb)_{cent.}$ angles are much weaker and equal to $108.22(9)$ and $112.03(9)^\circ$, respectively. The shortest distance between the two centroids of the aromatic cycles of the bidentate $o-Me_2N-C_6H_4CH_2$ ligands is equal to 3.792 Å, pointing out an intramolecular π -stacking interaction. Analysis of the crystal packing indicates that the shortest intermolecular $Dy-Dy$ distance is equal to $10.1740(7)$ Å, suggesting that the complexes are relatively well isolated (Figure S1).

The magnetic properties were investigated in both, static and dynamic modes by using a SQUID MPMS-XL. At room temperature, the χT value of $14.03 \text{ cm}^3 \cdot K \cdot \text{mol}^{-1}$ for **1** is in an excellent accordance with the value of $14.17 \text{ cm}^3 \cdot K \cdot \text{mol}^{-1}$, expected for a unique Dy^{3+} ion using the free-ion approximation (Figure S2). Reducing the temperature induces a monotonous decrease of χT , reflecting the thermal depopulation of the $\pm m_J$ levels.

Figure 1. a) Molecular structure of **1**. Color code: orange, Dy; grey, C; blue, N. Hydrogen atoms have been omitted for clarity. The dashed green bond indicates the $Dy \cdots (tBu_4Carb)_{cent.}$ interaction. b) Top view of the molecular structure of **1**.

Below 10 K, a dramatic χT decrease is observed to reach the value of $5.24 \text{ cm}^3 \cdot K \cdot \text{mol}^{-1}$ at 1.8 K. The field dependence of the magnetization monitored at 1.8 K shows the characteristic unsaturated curve with a value of $5.13 N\beta$ under a 70 kOe field. Besides, a clear inflection point could be observed at low field and was previously observed in other lanthanide based SMMs.^{6b, 6e, 17, 21} Such phenomenon may express either the extreme field dependence of the relaxation rates^{6b} or the flip of the Dy^{3+} spins under an applied magnetic field.¹⁷ At low temperature, a clear opening in the hysteresis loop could be evidenced (Figure S3), suggesting the occurrence of a slow relaxation of the magnetization.

Such fact was further corroborated by using alternate current (ac) measurements with the aim to analyze the relaxation dynamic. Under a zero dc-field, **1** exhibits a clear frequency dependence of the in-phase (χ') and out-of-phase (χ'') components of the magnetic susceptibility (Figure 2), pointing out a SMM behavior. A single frequency peak of χ'' that shifts towards higher frequency as the temperature increases could be noticed (Figure 2), while these out-of-phase signals could be observed up to 45 K (Figure S4). The related Cole-Cole plots (Figure S5), fitted with a generalized Debye model, give moderate α parameter values (< 0.18 ; Table S2). This latter being directly associated to the distribution of relaxation times, the program *CC-FIT2*, recently developed by *Reta and Chilton*,²² was utilized to extract the relaxation time (τ) values and the corresponding uncertainties from the underlying distribution function.

The temperature dependence of the relaxation time (Figure 3) reveals an overlap between different relaxation processes. Attempts to fit the data were performed by considering the following

equation: $\tau^{-1} = \tau_0^{-1} \exp(-\Delta/kT) + CT^n + \tau_{\text{QTM}}^{-1}$ (Eq. 1),²³ for which the first term accounts for a thermally activated process, while the second and third ones stand for two-phonon Raman and QTM, respectively. By taking into account the simple extracted τ values or the distribution of relaxation time (CC-FIT2), small Δ barriers and/or large uncertainties were obtained. This suggests that the thermally activated Orbach process is not dominant or even not involved in the relaxation in the investigated temperature range. The fitting was therefore performed considering only a Raman and QTM processes $\tau^{-1} = CT^n + \tau_{\text{QTM}}^{-1}$ (Eq. 2) and gives the parameters found in Table 1. For comparison, the parameters obtained from CCFIT2 are reported in Table S3.

At low temperature, the relaxation time starts to become temperature independent indicating a significant QTM contribution. This latter could be shortcut by applying dc magnetic fields. Consequently, the field dependence of the ac susceptibilities was investigated for various fields up to 6000 Oe (Figure S6). The corresponding field dependence of the relaxation time could be modeled with, $\tau^{-1} = DH^4T + B_1/(1+B_2H^2) + K$ (Eq. 3), for which the first term accounts for the direct process (for Kramers-ion), the second one for the QTM, while the K constant accounts for Raman and thermally activated processes (Figure S7, Table S4). A maximum increase of the relaxation time is observed for an optimum field of 1000 Oe. When measured under this dc field, out-of-phase peaks could be observed up to 27 K confirming the decrease of the QTM (Figure S8). The Cole-Cole plots (Figure S9), fitted with a general Debye model, give reduced values of the α parameter (< 0.06 ; Table S5) with respect to the zero-field data and smaller uncertainties related to the relaxation time (Figure 3).

Figure 2. Frequency dependence of the out-of phase (χ'') susceptibilities for **1** under a zero dc-field.

Attempts to fit the temperature dependence of the relaxation time considering only a Raman process was performed (Figure S10, Table S3), considering that the direct process should be inoperative for such weak values of magnetic field. However, a

better fit could be obtained by adding a thermally activated process as $\tau^{-1} = \tau_0^{-1} \exp(-\Delta/kT) + CT^n$ (Eq. 4) (Figure 3, Table 1). To avoid over-parameterization, the n parameter was successively fixed to different values until getting the best fitting coefficient. In contrast to the zero-field data, the shortcut of the QTM reveals the Orbach process in a higher temperature range.

Magneto-structural correlations could be achieved by determining the orientation of the anisotropic axis for the ground Kramers doublet of **1** by using the MAGELLAN software.²⁴ The negative charge on the *t*Bu₄Carb ligand was delocalized on the five atoms of the heterocycle, whereas two negative charges were ascribed on each bonded carbons of the *o*-Me₂N-C₆H₄CH₂ ligands. It turns out that the η^5 -carbazolyl ligand imposes the direction of the anisotropic axis, which is found to pass almost through the centroid of the five-membered heterocycle (deviation of about 5°, Figure S11). As a consequence, it appears that the C35-Dy-C44 sequence showing comparable Dy-ligand distances but an angle of 138.5°, which strongly deviates from linearity, is not favorable to dominate the electrostatic contribution. However, these negatively charged carbons localized almost perpendicular to the anisotropic axis most likely create a transverse component explaining the occurrence of the substantial QTM contribution. This latter precludes the observation of a thermally activated process under a zero-dc field. The relaxation is therefore dominated by both Raman and QTM. However, applying dc fields causes a shift of the ac signals towards higher temperatures and reveals a thermally activated relaxation.

Table 1: Fit parameters of the temperature dependence of the relaxation time for **1**.

Compound	Δ (cm ⁻¹)	τ_0 (s)	n	C (s ⁻¹ .K ⁻ⁿ)	τ_{QTM} (s)
1 (0 Oe)	-	-	2.7 ± 0.1	0.7 ± 0.3	0.00057 ± 0.00002
1 (1000 Oe)	50 ± 1	(4.47 ± 0.06) × 10 ⁻⁵	4.1 *	0.0023 ± 0.0002	-

*fixed parameter

Figure 3. Temperature dependence of the relaxation time, τ , for **1**. The uncertainties were determined from the CC-FIT2 software.²² The red solid lines correspond to the fit with Eq. 2 (0 Oe) and Eq. 4 (1000 Oe).

We have reported in this communication the synthesis and structure of a new heteroleptic Dy(III) complex based on carbazolyl and carbanions ligands. Remarkably, a η^5 -coordinated mode carbazolyl ligand is observed for the first time

with a lanthanide(III) ion. This coordination mode results in a complex with a relatively high axial crystal-field, able to stabilize the oblate electronic density of Dy(III), which leads to a genuine SMM behavior. While the relaxation in zero-field occurs through a combination of Raman and QTM processes due to the presence of coordinated ligands in the equatorial plane, the application of dc field suppresses the QTM and reveals Raman and thermally activated relaxations. Such carbazolyl ligands may therefore be considered as promising alternatives to usual Cp ligands to design high-energy barriers SMMs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, additional structural and magnetic data could be found in the PDF.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jerome.long@umontpellier.fr

*E-mail: trif@iomc.ras.ru

Author Contributions

†All the authors contributed equally.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

The financial support of the Russian Science Foundation is highly acknowledged (Project № 17-73-30036). The French authors thank the University of Montpellier, CNRS and PAC of ICGM.

REFERENCES

- (1) (a) Luzon, J.; Sessoli, R., Lanthanides in molecular magnetism: so fascinating, so challenging. *Dalton Trans.* **2012**, 41 (44), 13556-13567; (b) Woodruff, D. N.; Winpenny, R. E. P.; Layfield, R. A., Lanthanide single-molecule magnets. *Chem. Rev.* **2013**, 113 (7), 5110-5148; (c) Troiani, F.; Affronte, M., Molecular spins for quantum information technologies. *Chem. Soc. Rev.* **2011**, 40 (6), 3119-3129; (d) Bogani, L.; Wernsdorfer, W., Molecular spintronics using single-molecule magnets. *Nat. Mater.* **2008**, 7 (3), 179-186.
- (2) Giansiracusa, M. J.; Kostopoulos, A. K.; Collison, D.; Winpenny, R. E. P.; Chilton, N. F., Correlating blocking temperatures with relaxation mechanisms in monometallic single-molecule magnets with high energy barriers (Ueff > 600 K). *Chem. Commun.* **2019**, 55 (49), 7025-7028.
- (3) (a) Ungur, L.; Chibotaru, L. F., Strategies toward High-Temperature Lanthanide-Based Single-Molecule Magnets. *Inorg. Chem.* **2016**, 55 (20), 10043-10056; (b) Liu, J.-L.; Chen, Y.-C.; Tong, M.-L., Symmetry strategies for high performance lanthanide-based single-molecule magnets. *Chem. Soc. Rev.* **2018**, 47 (7), 2431-2453; (c) Tang, J.; Zhang, P., Lanthanide Single-Ion Molecular Magnets. In *Lanthanide Single Molecule Magnets*, Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; pp 41-90; (d) Layfield, R. A.; Murugesu, M., *Lanthanides and Actinides in Molecular Magnetism*. Wiley: 2015.
- (4) Chilton, N. F., Design Criteria for High-Temperature Single-Molecule Magnets. *Inorg. Chem.* **2015**, 54 (5), 2097-2099.
- (5) Rinehart, J. D.; Long, J. R., Exploiting single-ion anisotropy in the design of f-element single-molecule magnets. *Chem. Sci.* **2011**, 2 (11), 2078-2085.
- (6) (a) Liu, J.; Chen, Y.-C.; Liu, J.-L.; Vieru, V.; Ungur, L.; Jia, J.-H.; Chibotaru, L. F.; Lan, Y.; Wernsdorfer, W.; Gao, S.; Chen, X.-M.; Tong, M.-L., A Stable Pentagonal Bipyramidal Dy(III) Single-Ion Magnet with a Record Magnetization Reversal Barrier over 1000 K. *J. Am. Chem. Soc.* **2016**, 138 (16), 5441-5450; (b) Gupta, S. K.; Rajeshkumar, T.; Rajaraman, G.; Murugavel, R., An air-stable Dy(III) single-ion magnet with high anisotropy barrier and blocking temperature. *Chem. Sci.* **2016**, 7 (8), 5181-5191; (c) Gregson, M.; Chilton, N. F.; Ariciu, A.-M.; Tuna, F.; Crowe, I. F.; Lewis, W.; Blake, A. J.; Collison, D.; McInnes, E. J. L.; Winpenny, R. E. P.; Liddle, S. T., A monometallic lanthanide bis(methanediide) single molecule magnet with a large energy barrier and complex spin relaxation behaviour. *Chem. Sci.* **2016**, 7 (1), 155-165; (d) Chen, Y.-C.; Liu, J.-L.; Ungur, L.; Liu, J.; Li, Q.-W.; Wang, L.-F.; Ni, Z.-P.; Chibotaru, L. F.; Chen, X.-M.; Tong, M.-L., Symmetry-Supported Magnetic Blocking at 20 K in Pentagonal Bipyramidal Dy(III) Single-Ion Magnets. *J. Am. Chem. Soc.* **2016**, 138 (8), 2829-2837; (e) Ding, Y.-S.; Chilton, N. F.; Winpenny, R. E. P.; Zheng, Y.-Z., On Approaching the Limit of Molecular Magnetic Anisotropy: A Near-Perfect Pentagonal Bipyramidal Dysprosium(III) Single-Molecule Magnet. *Angew. Chem. Int. Edit.* **2016**, 55 (52), 16071-16074; (f) Meng, Y.-S.; Xu, L.; Xiong, J.; Yuan, Q.; Liu, T.; Wang, B.-W.; Gao, S., Low-Coordinate Single-Ion Magnets by Intercalation of Lanthanides into a Phenol Matrix. *Angew. Chem. Int. Edit.* **2018**, 57 (17), 4673-4676; (g) Canaj, A. B.; Dey, S.; Martí, E. R.; Wilson, C.; Rajaraman, G.; Murrie, M., Insight into D6h Symmetry: Targeting Strong Axiality in Stable Dysprosium(III) Hexagonal Bipyramidal Single-Ion Magnets. *Angew. Chem. Int. Edit.* **2019**, 58 (40), 14146-14151; (h) Ding, Y. S.; Han, T.; Zhai, Y. Q.; Reta, D.; Chilton, N. F.; Winpenny, R. E. P.; Zheng, Y. Z., A Study of Magnetic Relaxation in Dysprosium(III) Single-Molecule Magnets. *Chem. Eur. J.* **2020**, 26 (26), 5893-5902.
- (7) (a) Guo, F. S.; Day, B. M.; Chen, Y. C.; Tong, M. L.; Mansikkamäki, A.; Layfield, R. A., A Dysprosium Metallocene Single-Molecule Magnet Functioning at the Axial Limit. *Angew. Chem. Int. Ed. Engl.* **2017**, 56 (38), 11445-11449; (b) Goodwin, C. A. P.; Ortu, F.; Reta, D.; Chilton, N. F.; Mills, D. P., Molecular magnetic hysteresis at 60 kelvin in dysprosocenium. *Nature* **2017**, 548 (7668), 439-442; (c) Randall McClain, K.; Gould, C. A.; Chakarawet, K.; Teat, S. J.; Groshens, T. J.; Long, J. R.; Harvey, B. G., High-temperature magnetic blocking and magneto-structural correlations in a series of dysprosium(III) metallocenium single-molecule magnets. *Chem. Sci.* **2018**, 9 (45), 8492-8503.
- (8) Guo, F.-S.; Day, B. M.; Chen, Y.-C.; Tong, M.-L.; Mansikkamäki, A.; Layfield, R. A., Magnetic hysteresis up to 80 kelvin in a dysprosium metallocene single-molecule magnet. *Science* **2018**, 362 (6421), 1400-1403.
- (9) (a) Le Roy, J. J.; Jeletic, M.; Gorelsky, S. I.; Korobkov, I.; Ungur, L.; Chibotaru, L. F.; Murugesu, M., An Organometallic Building Block Approach To Produce a Multidecker 4f Single-Molecule Magnet. *J. Am. Chem. Soc.* **2013**, 135 (9), 3502-3510; (b) Ungur, L.; Le Roy, J. J.; Korobkov, I.; Murugesu, M.; Chibotaru, L. F., Fine-tuning the Local Symmetry to Attain Record Blocking Temperature and Magnetic Remanence in a Single-Ion Magnet. *Angew. Chem., Int. Ed.* **2014**, 53 (17), 4413-4417; (c) Le Roy, J. J.; Ungur, L.; Korobkov, I.; Chibotaru, L. F.; Murugesu, M., Coupling strategies to enhance single-molecule magnet properties of erbium-cyclooctatetraenyl complexes. *J. Am. Chem. Soc.* **2014**, 136 (22), 8003-8010; (d) Jiang, S.-D.; Wang, B.-W.; Sun, H.-L.; Wang, Z.-M.; Gao, S., An Organometallic Single-Ion Magnet. *J. Am. Chem. Soc.* **2011**, 133 (13), 4730-4733; (e) Meihäus, K. R.; Long, J. R., Magnetic Blocking at 10 K and a Dipolar-Mediated Avalanche in Salts of the Bis(η⁸-cyclooctatetraenide) Complex [Er(COT)₂]. *J. Am. Chem. Soc.* **2013**, 135 (47), 17952-17957; (f) Harriman, K. L. M.; Le Roy, J. J.; Ungur, L.; Holmberg, R. J.; Korobkov, I.; Murugesu, M., Cycloheptatrienyl trianion: an elusive bridge in the search of exchange coupled dinuclear organolanthanide single-molecule magnets. *Chem. Sci.* **2017**, 8 (1), 231-240; (g) Kilpatrick, A. F. R.; Guo, F.-S.; Day, B. M.; Mansikkamäki, A.; Layfield, R. A.; Cloke, F. G. N., Single-molecule magnet properties of a monometallic dysprosium pentalene complex. *Chem. Commun.* **2018**, 54 (51), 7085-7088.
- (10) Kotrlé, K.; Herchel, R., Are Inorganic Single-Molecule Magnets a Possibility? A Theoretical Insight into Dysprosium Double-Deckers with Inorganic Ring Systems. *Inorg. Chem.* **2019**, 58 (20), 14046-14057.
- (11) Evans, P.; Reta, D.; Whitehead, G. F. S.; Chilton, N. F.; Mills, D. P., Bis-Monophospholyl Dysprosium Cation Showing Magnetic Hysteresis at 48 K. *J. Am. Chem. Soc.* **2019**, 141 (50), 19935-19940.
- (12) Jin, P.-B.; Zhai, Y.-Q.; Yu, K.-X.; Winpenny, R. E. P.; Zheng, Y.-Z., Dysprosiacarboranes as Organometallic Single-Molecule Magnets. *Angew. Chem. Int. Edit.* **2020**, 59 (24), 9350-9354.
- (13) Kays, D. L., Extremely bulky amide ligands in main group chemistry. *Chem. Soc. Rev.* **2016**, 45 (4), 1004-1018.
- (14) (a) Kong, F. K.-W.; Tang, M.-C.; Wong, Y.-C.; Chan, M.-Y.; Yam, V. W.-W., Design Strategy for High-Performance Dendritic Carbazole-Containing Alkynylplatinum(II) Complexes and Their

- Application in Solution-Processable Organic Light-Emitting Devices. *J. Am. Chem. Soc.* **2016**, *138* (19), 6281-6291; (b) Shi, S.; Jung, M. C.; Coburn, C.; Tadde, A.; Sylvinson M. R. D.; Djurovich, P. I.; Forrest, S. R.; Thompson, M. E., Highly Efficient Photo- and Electroluminescence from Two-Coordinate Cu(I) Complexes Featuring Nonconventional N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2019**, *141* (8), 3576-3588; (c) Hamze, R.; Shi, S.; Kapper, S. C.; Muthiah Ravinson, D. S.; Estergreen, L.; Jung, M.-C.; Tadde, A. C.; Haiges, R.; Djurovich, P. I.; Peltier, J. L.; Jazsar, R.; Bertrand, G.; Bradforth, S. E.; Thompson, M. E., "Quick-Silver" from a Systematic Study of Highly Luminescent, Two-Coordinate, d10 Coinage Metal Complexes. *J. Am. Chem. Soc.* **2019**, *141* (21), 8616-8626.
- (15) (a) Long, J.; Guari, Y.; Ferreira, R. A. S.; Carlos, L. D.; Larionova, J., Recent advances in luminescent lanthanide based Single-Molecule Magnets. *Coord. Chem. Rev.* **2018**, *363*, 57-70; (b) Jia, J.-H.; Li, Q.-W.; Chen, Y.-C.; Liu, J.-L.; Tong, M.-L., Luminescent single-molecule magnets based on lanthanides: Design strategies, recent advances and magneto-luminescent studies. *Coord. Chem. Rev.* **2019**, *378*, 365-381.
- (16) (a) Müller-Buschbaum, K.; Quitmann, Catharina C., Homoleptic Rare-Earth Carbazolates and the Trends of Their E Redox Potentials: Mixed-Valent Samarium in $1\infty[\text{Sm}2(\text{Cbz})5](\text{CbzH})$ (CbzH = carbazole) and Trivalent Thulium, Neodymium and Gadolinium in $[\text{Ln}2(\text{Cbz})6]$. *Eur. J. Inorg. Chem.* **2004**, *2004* (21), 4330-4337; (b) Evans, W. J.; Rabe, G. W.; Ziller, J. W., Stereochemical Variability in Samarium(II) Reagents Using Carbazole as an Alternative to Iodide: Synthesis and Structure of $\text{cis}-(\text{C}_{12}\text{H}_8\text{N})_2\text{Sm}(\text{THF})_4$ and $\text{trans}-(\text{C}_{12}\text{H}_8\text{N})_2\text{Sm}(\text{N-MeIm})_4$. *Organometallics* **1994**, *13* (5), 1641-1645; (c) Müller-Buschbaum, K.; Zurawski, A., On the Mechanisms of Electride Induced Synthesis of Ytterbium Carbazolates, Formation of Coordination Polymers by Condensation and Polymer Degradation by Chemical Scissors. *Z. Anorg. Allg. Chem.* **2007**, *633* (13-14), 2300-2304.
- (17) Long, J.; Selikhov, A. N.; Mamontova, E.; Lyssenko, K. A.; Guari, Y.; Larionova, J.; Trifonov, A., Single-molecule magnet behavior in luminescent carbazolyl Dy(III) octahedral complexes with a quasi linear N-Dy-N angle. *Dalton Trans.* **2020**, *49* (13), 4039-4043.
- (18) (a) Selikhov, A. N.; Cherkasov, A. V.; Fukin, G. K.; Trifonov, A. A.; del Rosal, I.; Maron, L., Amido Analogues of Nonbent Lanthanide (II) and Calcium Metallocenes. Heterolytic Cleavage of π -Bond Ln-Carbazolyl Ligand Promoted by Lewis Base Coordination. *Organometallics* **2015**, *34* (3), 555-562; (b) Selikhov, A. N.; Mahrova, T. V.; Cherkasov, A. V.; Fukin, G. K.; Maron, L.; Trifonov, A. A., Half-Sandwich Alkyl, Amido, and Iodo Samarium(II) Complexes: Non-Conventional Sterically Governed Oxidation of $(\text{tBu}_4\text{Carb})_2\text{Sm}$. *Chem. Eur. J.* **2017**, *23* (6), 1436-1443; (c) Selikhov, A. N.; Shavyrin, A. S.; Cherkasov, A. V.; Fukin, G. K.; Trifonov, A. A., Thermally Stable Half-Sandwich Benzhydryl Ln(II) (Ln = Sm, Yb) Complexes Supported by Sterically Demanding Carbazolyl and Fluorenyl Ligands. *Organometallics* **2019**, *38* (24), 4615-4624.
- (19) Guo, Y.-N.; Ungur, L.; Granroth, G. E.; Powell, A. K.; Wu, C.; Nagler, S. E.; Tang, J.; Chibotaru, L. F.; Cui, D., An NCN-pincer ligand dysprosium single-ion magnet showing magnetic relaxation via the second excited state. *Sci. Rep.* **2014**, *4*, 5471.
- (20) Day, B. M.; Guo, F.-S.; Layfield, R. A., Cyclopentadienyl Ligands in Lanthanide Single-Molecule Magnets: One Ring To Rule Them All? *Acc. Chem. Res.* **2018**, *51* (8), 1880-1889.
- (21) Long, J.; Basalov, I. V.; Forosenko, N. V.; Lyssenko, K. A.; Mamontova, E.; Cherkasov, A. V.; Damjanović, M.; Chibotaru, L. F.; Guari, Y.; Larionova, J.; Trifonov, A. A., Dysprosium Single-Molecule Magnets with Bulky Schiff-base Ligands: Modification of the Slow Relaxation of the Magnetization by Substituent Change. *Chem. Eur. J.* **2019**, *25*, 474-478.
- (22) Reta, D.; Chilton, N. F., Uncertainty estimates for magnetic relaxation times and magnetic relaxation parameters. *Phys. Chem. Chem. Phys.* **2019**, *21* (42), 23567-23575.
- (23) Meihäus, K. R.; Minasian, S. G.; Lukens, W. W.; Kozimor, S. A.; Shuh, D. K.; Tyliczszak, T.; Long, J. R., Influence of pyrazolate vs N-heterocyclic carbene ligands on the slow magnetic relaxation of homoleptic trischelate lanthanide(III) and uranium(III) complexes. *J. Am. Chem. Soc.* **2014**, *136* (16), 6056-6068.
- (24) Chilton, N. F.; Collison, D.; McInnes, E. J. L.; Winpenny, R. E. P.; Soncini, A., An electrostatic model for the determination of magnetic anisotropy in dysprosium complexes. *Nat. Commun.* **2013**, *4*, 2551.