



## Synthesis, structure and magnetic properties of a series of Ln( iii ) complexes with radical-anionic iminopyridine ligands: effect of lanthanide ions on the slow relaxation of the magnetization

Jérôme Long, Grigorii Skvortsov, Anton Cherkasov, Konstantin A. Lyssenko, Andrei Poddel'Sky, Yannick Guari, Joulia Larionova, Alexander A. Trifonov

### ► To cite this version:

Jérôme Long, Grigorii Skvortsov, Anton Cherkasov, Konstantin A. Lyssenko, Andrei Poddel'Sky, et al.. Synthesis, structure and magnetic properties of a series of Ln( iii ) complexes with radical-anionic iminopyridine ligands: effect of lanthanide ions on the slow relaxation of the magnetization. Dalton Transactions, 2019, 48 (32), pp.12018-12022. 10.1039/C9DT00738E . hal-02270823

**HAL Id: hal-02270823**

**<https://hal.science/hal-02270823>**

Submitted on 26 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.

# Synthesis, structure and magnetic properties of a series of Ln(III) complexes with radical-anionic iminopyridine ligands: effect of the lanthanide ion over the slow relaxation of the magnetization.

Jérôme Long\*,<sup>a</sup> Grigori G. Skvortsov,<sup>b</sup> Anton V. Cherkasov,<sup>b</sup> Konstantin A. Lyssenko,<sup>c</sup> Andrei I. Poddel'sky,<sup>b</sup> Yannick Guari,<sup>a</sup> Joulia Larionova<sup>a</sup> and Alexander A. Trifonov\*<sup>b,c</sup>

**We report the synthesis, structure and magnetic properties investigation of a series of homoleptic Ln(III) complexes coordinated by radical-anionic iminopyridine ligands of general formula [Ln(IPy)<sub>3</sub>]-solv (IPy = iminopyridine; Ln = Tb, Dy, Er, Y, Gd). The dysprosium analogue exhibits a zero-field Single-Molecule Magnet (SMM) behavior.**

Owing to their exceptional magnetic properties, lanthanide coordination and organometallic chemistries have recently taken a decisive turn in materials science. In this line of thought, Single-Molecule Magnets (SMMs) based on lanthanide ions have totally changed the molecular magnetism landscape and are often considered as future candidates for high-density information storage or quantum computing.<sup>1-4</sup> In such complexes, the high magnetic anisotropy of the lanthanide ion in a particular environment gives rise to the appearance of an energy barrier,  $\Delta$ , separating two opposites magnetic states and resulting in a superparamagnetic behaviour.

Yet, designing high performance SMMs requires to accurately control the coordination environment of the lanthanide ions in order to maximize the anisotropy and crystal-field splitting, while minimizing the Quantum Tunnelling of the Magnetization (QTM). This latter provides underbarrier relaxation pathways that limit the SMM performances, such as the energy barrier and magnetic coercivity. Although the physical origin with respect to QTM is different, Raman and direct processes provide also underbarrier relaxations that reduce the capacity of the SMMs. The coordination environment around the lanthanide ion depends on both electronic and symmetry considerations generated by the contiguous ligands. Taking advantage of this strategy, several lanthanide complexes exhibiting very high anisotropic barriers of few thousands of  $\text{cm}^{-1}$  have been reported within the last few years,<sup>5-9</sup> while a dysprosium metallocene complexes shows a high temperature hysteresis<sup>8, 10-11</sup> or that could even overcome liquid nitrogen's boiling temperature.<sup>12</sup>

Although QTM is known to depend on symmetry, dipolar and hyperfine interactions,<sup>13</sup> the presence of intermolecular exchange interactions could greatly influence the relaxation dynamics in a complex fashion. On one hand, sometimes the presence of a neighbouring paramagnetic centre to the lanthanide site can produce an internal field that could suppress the tunnelling.<sup>14</sup> On the other hand, enhancement of the relaxation dynamics has also been observed in dinuclear systems exhibiting crystallographically independent lanthanide

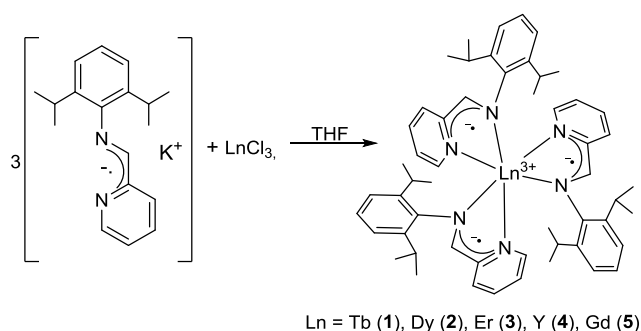
sites due to the creation of a local transverse magnetic moment.<sup>15-16</sup> In addition, the strength of the exchange interaction also influences the energy splitting between the ground and excited states in polynuclear systems which should be as high as large as possible to obtain large energy barrier systems. With this in mind, several exchange biased systems showing genuine SMM behaviour have been reported.<sup>17-19</sup>

Due to the intern character of the *f* orbitals, radical ligands could be viewed as particularly appropriate to promote significant interactions and study the influence over the slow relaxation of the magnetization.<sup>20</sup> Many lanthanide-based systems containing miscellaneous radical ligands, such as nitronyl nitroxides,<sup>21-22</sup> oxidized phthalocyanine,<sup>23</sup> semiquinones,<sup>24</sup> verdazyls,<sup>25</sup> triazinyl,<sup>26</sup> bipyrimidyl,<sup>27</sup> pyridyl-pyrazine,<sup>28</sup> indigo,<sup>29</sup> or dinitrogen have been reported.<sup>30</sup> For instance, the latest example has hold the record for the highest coercivity of 14 K for many years.<sup>30</sup>

Among radical-lanthanide systems with great potentialities, ytterbium-radical metallocenes with various heterocyclic amines have been studied.<sup>31</sup> Remarkably, an exchange coupling larger than hundreds of  $\text{cm}^{-1}$  has been reported in several ytterbium metallocenes complexes.<sup>32-33</sup> Despite such advantages, the investigation has been solely dedicated to ytterbium-based complexes and the use of highly anisotropic Kramers ions, such as  $\text{Dy}^{3+}$  or  $\text{Er}^{3+}$ , particularly suitable to design SMMs has not been investigated. For instance, iminopyridines (IPy) belong to redox active ligands, but their coordination chemistry with such anisotropic lanthanide ions remains unexplored. Their great tunability in terms of both, steric and electronic properties, allows tailoring the coordination environment of the lanthanide site. In recent years, the reactions of various ytterbocenes with diimino ligands bearing various substituents were reported.<sup>34-38</sup> Among these complexes, a paramagnetic homoleptic  $\text{Yb}^{3+}$  complex coordinated by three iminopyridyl radical-anions has been obtained through the oxidative cleavage of the  $\eta^5\text{-Yb-Cp}$  bond (Cp = cyclopentadienyl). This complex shows a reduced magnetic moment at room temperature that suggests a strong radicals/ytterbium antiferromagnetic interaction.<sup>39</sup>

Following this, we report in this communication the synthesis, structure and magnetic studies of four homoleptic lanthanide complexes based on iminopyridine (lpy) ligands. Remarkably, the dysprosium analogue reveals a zero-field slow relaxation reflecting a genuine SMM behaviour.

Complexes  $\text{Ln}(\text{IPy}^-)_3$  ( $\text{Ln} = \text{Tb}$  (**1**),  $\text{Dy}$  (**2**),  $\text{Er}$  (**3**),  $\text{Y}$  (**4**),  $\text{Gd}$  (**5**)) were prepared by treating the potassium derivative of the related iminopyridine with  $\text{LnCl}_3$  in 3:1 molar ratio (Scheme 1).

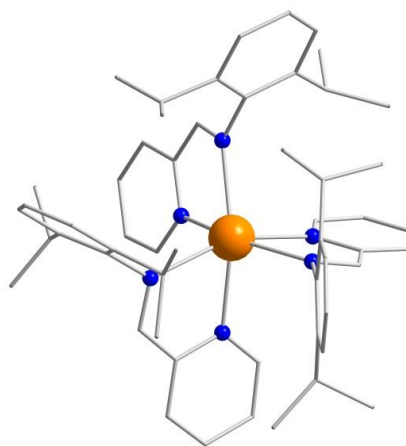


**Scheme 1.** Synthesis of complexes **1–5**.

Complexes **1–5** were obtained as moisture and air-sensitive dark green crystalline solids in 75, 72, 70, 73 and 71 % yields, respectively. X-Ray single crystal diffraction analysis (Fig. 1, Table S1) shows that compounds **1–5** crystallize in the hexagonal  $R\bar{3}$  space group as the solvates **1**·0.5(THF), **2**·0.5(Toluene), **3**·0.5(Toluene) and **4**·0.5(Toluene) and **5**·0.5(toluene). For the sake of clarity, only the crystal structure of **2** will be described. The molecular structure of **2** is shown in Figure 1. The coordination sphere is composed of six nitrogen atoms giving a hexacoordinated geometry close to a distorted octahedron as indicated by the SHAPE<sup>40</sup> analysis (Table S2). The Dy– $\text{N}_{\text{py}}$  distance of 2.424(2) Å is slightly longer than Dy– $\text{N}_{\text{imine}}$  one of 2.392(2) Å. The bonding situation within the planar diimino fragment  $\text{N}_{\text{py}}\text{--C--C--N}_{\text{imine}}$  in **2** is consistent with the radical anionic form of the ligand ( $\text{N}_{\text{imine}}\text{--C}$  1.339(3) Å;  $\text{C--C}$  1.394(3) Å;  $\text{N}_{\text{py}}\text{--C}$  1.383(2) Å).<sup>34</sup> The crystal packing shows that the shortest intermolecular distance Dy–Dy is equal to 8.306(2) Å, while no H-bonds have been detected (Fig. S1).

The radical-anionic nature of the iminopyridine ligands was further confirmed with Electron Paramagnetic Resonance (EPR) spectroscopy. While complexes **1–3** do not exhibit an observable EPR spectrum, **4** incorporating the diamagnetic  $\text{Y}^{3+}$  exhibits a broad line ( $\Delta E = 62$  G) at room temperature with  $g = 2.002$  without any hyperfine splitting and visible anisotropy (Fig. S2). The  $g$ -factor value is typical for ligand-centered radicals.

The radical-anionic nature of the ligands was also corroborated by the direct current (dc) magnetic properties' investigations of **4** incorporating the diamagnetic  $\text{Y}^{3+}$  ion, which exhibits intra- and intermolecular antiferromagnetic interactions between the radicals ( $S = \frac{1}{2}$ ) (Fig. S3, see ESI for details). The  $\chi T$  vs  $T$  curves for **1–5** show a gradual then abrupt decrease from around 30 K, most likely associated with the thermal depopulation of the  $\pm m_j$  levels from the  $\text{Ln}^{3+}$  ions combined with intra and intermolecular antiferromagnetic interactions (Fig. S3). The dc study of **5** presenting isotropic  $\text{Gd}^{3+}$  ion reveals that the intramolecular radical-radical interactions seem to be much greater than the  $\text{Gd}^{3+}$ -radical ones.



**Fig. 1.** Molecular structure of **2**. Colour code: orange, Dy; blue, N; grey, C; Hydrogen atoms have been omitted for clarity.

The slow relaxation of the magnetization was investigated by alternate currents (ac) measurements. Under a zero dc field, only the dysprosium analogue **2** shows a significant signal of out-of-phase susceptibility ( $\chi''$ ) component. The frequency dependence of  $\chi''$  at different temperatures shows the presence of a broad single peak (Fig. 2). Such out-of-phase signals could be observed up to 30 K on the temperature dependence of the ac susceptibilities (Fig. S4). Fitting of the Cole-Cole plots (Fig. S5) with a generalized Debye model show large values of the  $\alpha$  parameter (*i.e.* 0.42) at low temperature, indicating an important distribution of relaxation times (Table S3). Further insights into the relaxation dynamics could be obtained by analysing the temperature dependence of the relaxation time,  $\tau$ . A clear deviation from the linearity could be observed at low temperature, pointing out a divergence from a thermally activated process. Hence, the all data range could be modelled using the following equation:  $\tau^{-1} = \tau_0^{-1} \exp(-\Delta/kT) + CT^m + \tau_{\text{QTM}}^{-1}$  (Eq. 1).<sup>41</sup> The first term accounts for a thermally activated process, while the second and third ones stand for two-phonon Raman and QTM, respectively.

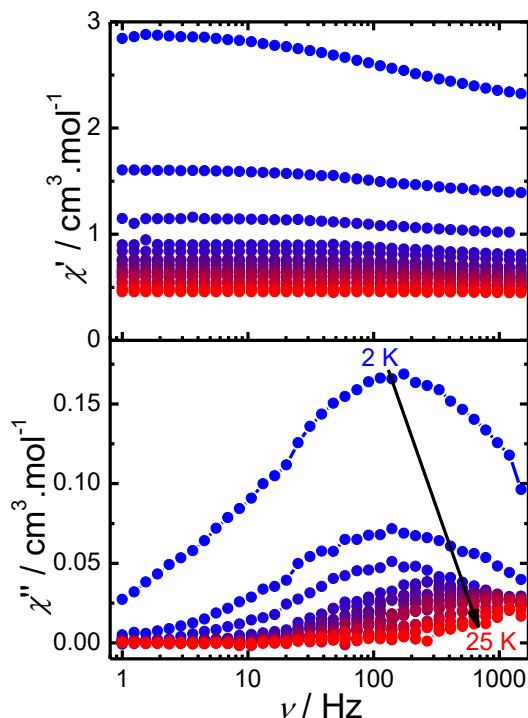


Fig. 2. Frequency dependence of  $\chi'$  and  $\chi''$  for **2** under a zero dc-field.

Surprisingly, the Raman process is found inoperative<sup>42</sup> and as a consequence, the magnetization relaxes through a combination of thermally activated and QTM processes (Table 1). Considering solely a Raman and QTM processes leads to poor fitting confirming that the relaxation involves readily a thermally activated relaxation. In order to shortcut this latter, the field dependence of the relaxation time was monitored at 15 K (Fig. S6). The complex behaviour could not be modelled with the usual equation  $\tau^{-1} = DH^4T + B_1/(1+B_2H^2) + K$  (Eq. 2), for which the first term accounts for the direct process (for Kramers-ion), the second one stands for the QTM, while the  $K$  constant accounts for the field-independent Raman and thermally activated process. However, the data clearly shows that the field showing the highest relaxation time is 1000 Oe. The frequency dependence of the ac susceptibilities under this dc field shows the presence of a broad peak for  $\chi''$  (Fig. S7-S8, Table S4), while the temperature dependence of  $\tau$  confirms the decrease of the QTM (Fig. 3). The temperature dependence of  $\tau$  could be fitted by taking into account an additional direct process:  $\tau^{-1} = \tau_0^{-1}\exp(-\Delta/kT) + CT^m + AT^n$  (Eq. 4). The value of  $\Delta$  (Table 1) is found comparable with respect to the zero-field data. The large distribution of the relaxation times may be explained by the presence of the crystallographic disorder of solvent molecules and/or ligands, as well as by impact of inter and intramolecular interactions. In contrast, the analogues **1** and **3** do not show a significant out-of-phase component even in the presence of a dc field (Fig. S9-S10). The observed behaviour follows the usual trend expected by electrostatic model and considering the angular dependence of the  $4f$  electronic density for the  $\text{Ln}^{3+}$  ions.<sup>43</sup>

Table 1: Fit parameters of the temperature dependence of the relaxation time for **2**.

Compound	$\Delta$ ( $\text{cm}^{-1}$ )	$\tau_0$ (s)	$m$	$C$ ( $\text{s}^{-1}.\text{K}^{-m}$ )	$\tau_{\text{QTM}}$ (ms)	$A$ ( $\text{s}^{-1}.\text{K}^{-1}$ )
<b>2</b> (0 Oe)	$28 \pm 4$	$(3 \pm 1) \times 10^{-5}$	9*	-	$1.0 \pm 0.1$	-
<b>2</b> (1000 Oe)	$34 \pm 3$	$(2.1 \pm 0.5) \times 10^{-6}$	9*	$(2.5 \pm 0.8) \times 10^{-10}$	-	$43 \pm 5$

While  $\text{Dy}^{3+}$  is a Kramers' oblate ion for which the electronic density could be stabilized by an axial crystal-field, the  $\text{Er}^{3+}$  ion Kramers ion exhibits a prolate density which could hardly be stabilized the IPy<sup>-</sup> ligands. On the other hand,  $\text{Tb}^{3+}$  is an oblate ion, however its non-Kramers nature (considering no exchange interaction) requires a particular geometry in order to observe a slow relaxation of the magnetization.<sup>44</sup> Since the presence of strong exchange interaction would modify the ground state, this suggests that the relaxation is mainly dominated by the single-ion anisotropy of the dysprosium rather than a coupled state with the radicals. This is in line with the observation of strong antiferromagnetic coupling between the radicals in **4** and **5**. In contrast to the strongly coupled  $\text{N}_2^{3-}$  radical bridged Tb complex, such lanthanide ion's dependence has been also observed in weakly exchange systems based on *r* bipyrimidyl or pyridyl-pyrazine ligands.<sup>27-28</sup> However, the presented systems exhibit a crystallographically imposed trigonal symmetry which should provide mixed  $m_j$  states. Although, zero-field slow relaxation in six-coordinate lanthanide complexes is rather scarce,<sup>45-47</sup> complex **2** is the first example of a zero-field undiluted SMM with such imposed symmetry. This suggests that despite being weak, the exchange interactions may affect the relaxation.

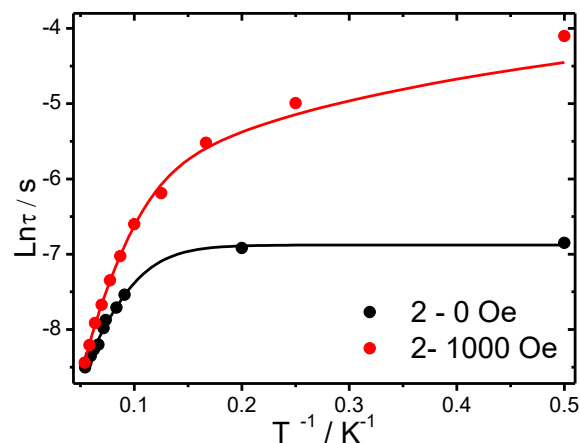


Fig. 3. Temperature dependence of the relaxation time for **2** using the ac susceptibility data at 0 Oe and 1000 Oe. The solid line represents the fit with Eq. 1 (0 Oe) or Eq. 3 (1000 Oe).

In summary, we have shown in this communication that the use of radical anion of IPy as ligand enables the formation of homoleptic magnetic complexes with a series of lanthanide ions. The study of the magnetic properties indicates that the dysprosium analogue shows a zero-field SMM behaviour for which out-of-phase signals could be still observed up to 30 K. The great tunability of such ligands in terms of both, steric and electronic factors should offer a careful tweaking of the

coordination environment in order to improve the slow relaxation features.

The authors thank the University of Montpellier, CNRS for financial support, PAC of ICGM for magnetic measurements and the Analytical Center of The G.A. Razuvaev IOMC RAS for the X-ray study. The Russian co-authors thank the Russian Science Foundation (grant 17-73-30036). The X-ray study of **2–4** has been carried out in the framework of the Russian state assignment (Theme № 44.2, Reg. № AAAA-A16-116122110053-1) using the equipment of The Analytical Center of IOMC RAS.

## Notes and references

- J. Luzon and R. Sessoli, *Dalton Trans.*, 2012, **41**, 13556-13567.
- D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113**, 5110-5148.
- F. Troiani and M. Affronte, *Chem. Soc. Rev.*, 2011, **40**, 3119-3129.
- L. Bogani and W. Wernsdorfer, *Nat. Mater.*, 2008, **7**, 179-186.
- J. Liu, Y.-C. Chen, J.-L. Liu, V. Vieru, L. Ungur, J.-H. Jia, L. F. Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, X.-M. Chen and M.-L. Tong, *J. Am. Chem. Soc.*, 2016, **138**, 5441-5450.
- S. K. Gupta, T. Rajeshkumar, G. Rajaraman and R. Murugavel, *Chem. Sci.*, 2016, **7**, 5181-5191.
- L. Ungur and L. F. Chibotaru, *Inorg. Chem.*, 2016, **55**, 10043-10056.
- F. S. Guo, B. M. Day, Y. C. Chen, M. L. Tong, A. Mansikkamäki and R. A. Layfield, *Angew. Chem. Int. Ed. Engl.*, 2017, **56**, 11445-11449.
- Y.-S. Ding, N. F. Chilton, R. E. P. Winpenny and Y.-Z. Zheng, *Angew. Chem. Int. Edit.*, 2016, **55**, 16071-16074.
- C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, *Nature*, 2017, **548**, 439-442.
- K. Randall McClain, C. A. Gould, K. Chakarawet, S. J. Teat, T. J. Groshens, J. R. Long and B. G. Harvey, *Chem. Sci.*, 2018, **9**, 8492-8503.
- F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki and R. A. Layfield, *Science*, 2018, **362**, 1400-1403.
- F. Pointillart, K. Bernot, S. Golhen, B. Le Guennic, T. Guizouarn, L. Ouahab and O. Cador, *Angew. Chem., Int. Ed.*, 2015, **54**, 1504-1507.
- S. T. Liddle and J. van Slageren, *Chem. Soc. Rev.*, 2015, **44**, 6655-6669.
- R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. L. McInnes, L. F. Chibotaru and R. E. P. Winpenny, *Nat. Chem.*, 2013, **5**, 673-678.
- E. Moreno Pineda, N. F. Chilton, R. Marx, M. Dörfel, D. O. Sells, P. Neugebauer, S.-D. Jiang, D. Collison, J. van Slageren, E. J. L. McInnes and R. E. P. Winpenny, *Nat. Comm.*, 2014, **5**, 5243.
- J. Long, F. Habib, P.-H. Lin, I. Korobkov, G. Enright, L. Ungur, W. Wernsdorfer, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.*, 2011, **133**, 5319-5328.
- K. Katoh, R. Asano, A. Miura, Y. Horii, T. Morita, B. K. Breedlove and M. Yamashita, *Dalton Trans.*, 2014, **43**, 7716-7725.
- S. Xue, Y.-N. Guo, L. Ungur, J. Tang and L. F. Chibotaru, *Chem. Eur. J.*, 2015, **21**, 14099-14106.
- S. Demir, I.-R. Jeon, J. R. Long and T. D. Harris, *Coord. Chem. Rev.*, 2015, **289-290**, 149-176.
- L. Bogani, C. Sangregorio, R. Sessoli and D. Gatteschi, *Angew. Chem. Int. Edit.*, 2005, **44**, 5817-5821.
- K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Am. Chem. Soc.*, 2006, **128**, 7947-7956.
- N. Ishikawa, M. Sugita, N. Tanaka, T. Ishikawa, S.-y. Koshihara and Y. Kaizu, *Inorg. Chem.*, 2004, **43**, 5498-5500.
- A. Caneschi, A. Dei, D. Gatteschi, S. Poussereau and L. Sorace, *Dalton Trans.*, 2004, DOI: 10.1039/B401144A, 1048-1055.
- L. Norel, L.-M. Chamoreau, Y. Journaux, O. Oms, G. Chastanet and C. Train, *Chem. Commun.*, 2009, DOI: 10.1039/B816910A, 2381-2383.
- I. S. Morgan, A. Mansikkamäki, M. Rouzies, R. Clerac and H. M. Tuononen, *Dalton Trans.*, 2017, **46**, 12790-12793.
- S. Demir, J. M. Zadrozny, M. Nippe and J. R. Long, *J. Am. Chem. Soc.*, 2012, **134**, 18546-18549.
- S. Demir, M. Nippe, M. I. Gonzalez and J. R. Long, *Chem. Sci.*, 2014, **5**, 4701-4711.
- F.-S. Guo and R. A. Layfield, *Chem. Commun.*, 2017, **53**, 3130-3133.
- J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *Nat. Chem.*, 2011, **3**, 538-542.
- C. H. Booth, M. D. Walter, D. Kazhdan, Y.-J. Hu, W. W. Lukens, E. D. Bauer, L. Maron, O. Eisenstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2009, **131**, 6480-6491.
- W. W. Lukens, N. Magnani and C. H. Booth, *Inorg. Chem.*, 2012, **51**, 10105-10110.
- C. H. Booth, D. Kazhdan, E. L. Werkema, M. D. Walter, W. W. Lukens, E. D. Bauer, Y.-J. Hu, L. Maron, O. Eisenstein, M. Head-Gordon and R. A. Andersen, *J. Am. Chem. Soc.*, 2010, **132**, 17537-17549.
- A. A. Trifonov, I. A. Borovkov, E. A. Fedorova, G. K. Fukin, J. Larionova, N. O. Druzhkov and V. K. Cherkasov, *Chem. - Eur. J.*, 2007, **13**, 4981-4987.
- A. A. Trifonov, *Eur. J. Inorg. Chem.*, 2007, **2007**, 3151-3167.
- M. D. Walter, D. J. Berg and R. A. Andersen, *Organometallics*, 2007, **26**, 2296-2307.
- K. Vasudevan and A. H. Cowley, *Chem. Commun.*, 2007, DOI: 10.1039/B708758F, 3464-3466.
- P. Cui, Y. Chen, G. Wang, G. Li and W. Xia, *Organometallics*, 2008, **27**, 4013-4016.
- A. A. Trifonov, E. A. Fedorova, I. A. Borovkov, G. K. Fukin, E. V. Baranov, J. Larionova and N. O. Druzhkov, *Organometallics*, 2007, **26**, 2488-2491.
- D. Casanova, M. Llunell, P. Alemany and S. Alvarez, *Chem. Eur. J.*, 2005, **11**, 1479-1494.
- K. R. Meihaus, S. G. Minasian, W. W. Lukens, S. A. Kozimor, D. K. Shuh, T. Tyliczszak and J. R. Long, *J. Am. Chem. Soc.*, 2014, **136**, 6056-6068.
- P. L. Scott and C. D. Jeffries, *Phys. Rev.*, 1962, **127**, 32-51.
- J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078-2085.
- N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Phys. Chem. B*, 2004, **108**, 11265-11271.
- S.-S. Liu, Y.-S. Meng, Y.-Q. Zhang, Z.-S. Meng, K. Lang, Z.-L. Zhu, C.-F. Shang, B.-W. Wang and S. Gao, *Inorg. Chem.*, 2017, **56**, 7320-7323.
- J.-L. Liu, K. Yuan, J.-D. Leng, L. Ungur, W. Wernsdorfer, F.-S. Guo, L. F. Chibotaru and M.-L. Tong, *Inorg. Chem.*, 2012, **51**, 8538-8544.
- M. Guo and J. Tang, *Inorganics*, 2018, **6**.