Building Axial Lanthanide Single-Molecule Magnets

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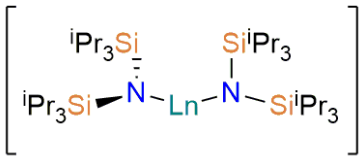
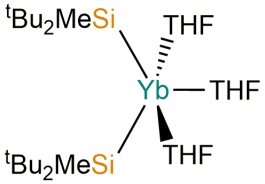
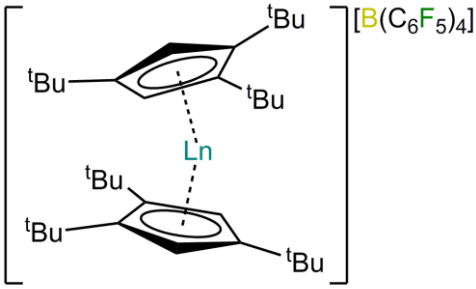
The complexity and richness of synthetic f-element chemistry has attracted increasing attention in recent years. This interest is stimulated jointly by scientific curiosity of a relatively unexplored field and the myriad applications that these elements have found in diverse areas such as organic synthesis, materials science and nuclear fuel cycles.[1] Our research focuses on stabilising lanthanide (Ln) and actinide (An) complexes with unusual coordination geometries and/or oxidation states, which can provide enhanced reactivity and unique physical properties, including interesting single-molecule magnet (SMM) behaviour in highly axial Ln complexes. We mainly utilise bulky bis(silyl)amides and cyclopentadienyls as supporting ligands to stabilise these unusual f-element motifs. Here we will present some recent highlights of this work, such as the first bent Ln(III) complexes (**1**),[2] the first quantification of Ln covalency using ^{29}Si NMR spectroscopy in the Yb(II) complex (**2**),[3] and isolated Ln(III) metallocenium cations (**3**), which provided record magnetic hysteresis temperatures for the dysprosium analogue in 2017 and new design criteria for high-performance SMMs.[4]



Ln = Sm, Tm, Yb [B(C6F5)4] **(1)**



(2)



Ln = Gd, Dy, Ho, Er, Tm, Yb, Lu **(3)**

References:

1. *The Lanthanides and Actinides*, Ed. S. T. Liddle, D. P. Mills, L. S. Natrajan, World Scientific Publishing Europe Ltd, Singapore, 2022.

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3. B. L. L. Réant, V. E. J. Berryman, A. R. Basford, L. E. Nodaraki, A. J. Wooles, F. Tuna, N. Kaltsoyannis, D. P. Mills, S. T. Liddle, *J. Am. Chem. Soc.*, 2021, **143**, 9813.

4. See for example: (a) C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, *Nature*, 2017, **548**, 439; (b) C. A. P. Goodwin, D. Reta, F. Ortu, N. F. Chilton and D. P. Mills, *J. Am. Chem. Soc.*, 2017, **139**, 18714; (c) P. Evans, D. Reta, G. F. S. Whitehead, N. F. Chilton and D. P. Mills, *J. Am. Chem. Soc.*, 2019, **141**, 19935.