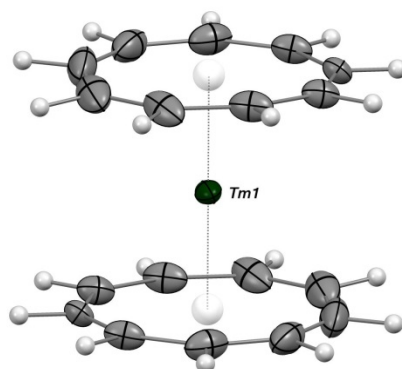


Symmetry control in divalent lanthanide chemistry: a challenge in synthesis, great spectroscopic interests

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Divalent lanthanide chemistry has remained for long a very confidential field and only a small number of precursors was available. Moreover these precursors were limited to “classical” divalent lanthanides (Eu, Yb and Sm).¹ This explain why preparing new precursors is of great interest for the field and their high reactivity can find application in the activation of inert small molecules. In contrary to the usual strategy in small molecule activation – using sterically hindered complexes to control the reactivity, we were interested to use less hindered precursors and therefore prepared the bis(triflate) complex of thulium (II).²

Having access to these new divalent precursor opened a new field for the spectroscopy studies of lanthanides. Whereas lanthanide spectroscopy is usually focusing on the trivalent oxidation state, we started studying the electronic properties of thulium (II).² We also managed to prepare the first divalent lanthanide single molecule magnet by a controlled set of ligand – and a rationalized crystalline field – around the metal centre.³



Thulocene complex

Another family of precursors was also prepared and studied: “sandwich”-like organometallic complexes. They were long limited to complexes bearing analogues of cyclopentadienyl or cyclooctatetraenyl ligands. These ligands were unfortunately not well fitted for divalent lanthanide chemistry because of their small size or their charge which prevented the preparation of neutral linear complexes. Using the mono-anionic nine-membered aromatic ring, also known as the cnt ligand, enabled us to prepare the first neutral, linear and divalent ytterbocene, samarocene and thulocene complexes.⁴ Complementary studies are in progress to understand the surprising stability of the complexes and their reactivity remains for the moment under studies.

[1] F. Nief, *Dalton Trans.*, **2010**, 39, 6589-6598

[2] M. Xémard, *et al.*, *Angew. Chem. Int. Ed.*, **2017**, 56, 4266-4271

[3] M. Xémard, *et al.*, *Inorg. Chem.*, **2019**, 58(4), 2872-2880

[4] M. Xémard, *et al.*, *J. Am. Chem. Soc.*, **2018**, 140(43), 14433-14439