Schiff base complexes derived from *N,N'*-bis(3-methoxysalicylidene)ethylene-1,2-diamine ligands for NIR luminescence and RNA cleavage

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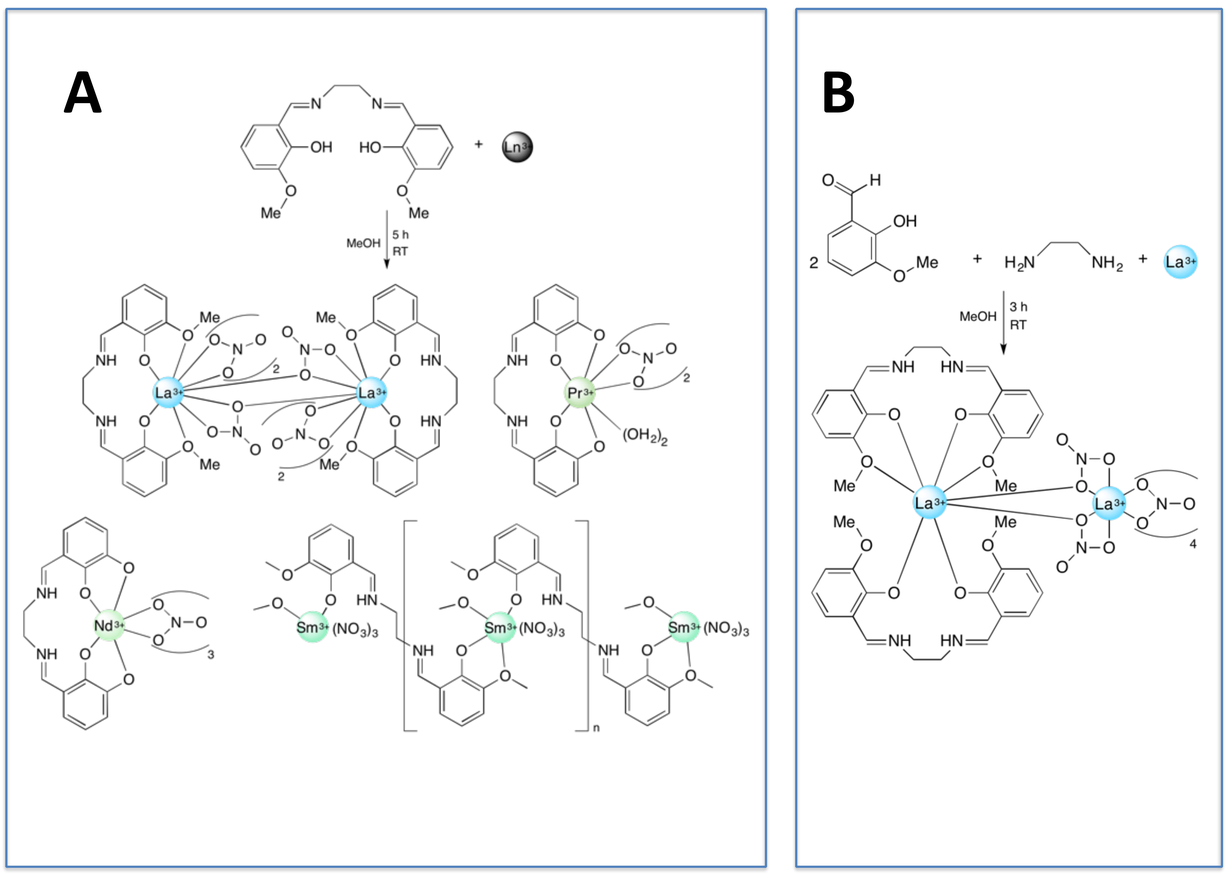
Introduction

Schiff base ligands are often referred to as "privileged ligands" because they can be obtained by simple self-condensation of a chosen aldehyde or ketone and primary amine precursor. These ligands also show good efficiency in binding with various metals (d-block metals, f-block metals, etc.).[1] Among the many interesting properties of lanthanide Schiff base complexes are their photoluminescence properties (both in the visible and near-infrared region NIR), catalytic activity, as well as ability to cleave RNA/DNA oligonucleotides.[2-3]

Research goal

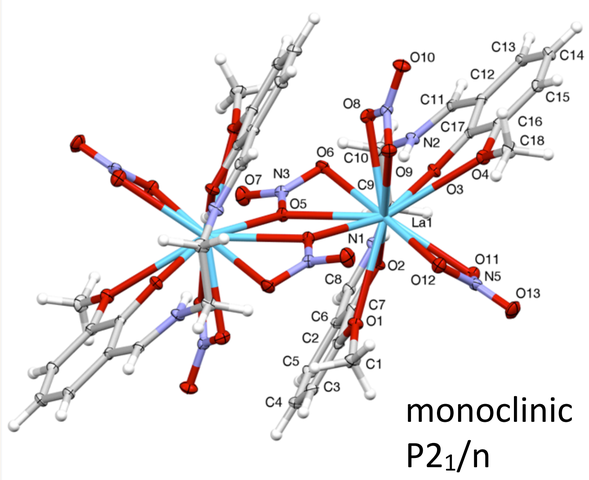
We investigated a series of ***lanthanide Schiff base salen-type complexes*** prepared using a ***bis-(3-methoxysalicilidene)ethylene-1,2-diamine ligand*** (Ln = La^{3+} - Lu^{3+}). The **ability to cleave** a **20-mer RNA** oligonucleotide: **5'-AGC-GAU-AAG-AUU-CAU-AUA-UC-3'** was investigated. Several of the complexes were also tested for the cleavage of **12-mer RNA** oligonucleotide with a sequence: **5'-GCA-CCC-UGU-CAG-3'**. A detailed **luminescence study** was additionally carried out and revealed that the **Nd^{3+}**, **Er^{3+}**, and **Yb^{3+}** complexes show strong emission in the near-infrared region.

Synthesis: (A) two-step and (B) one-pot

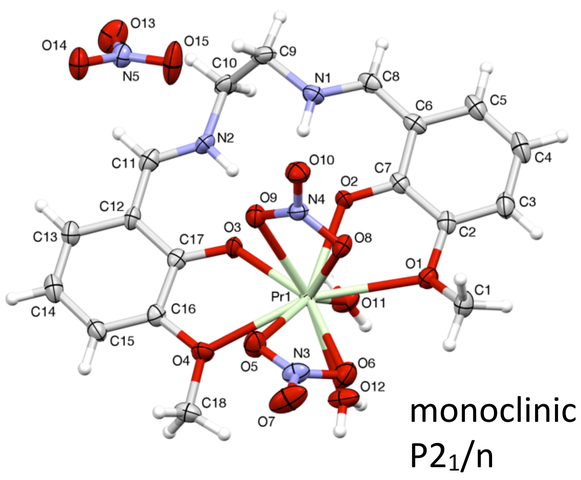


Crystal structures

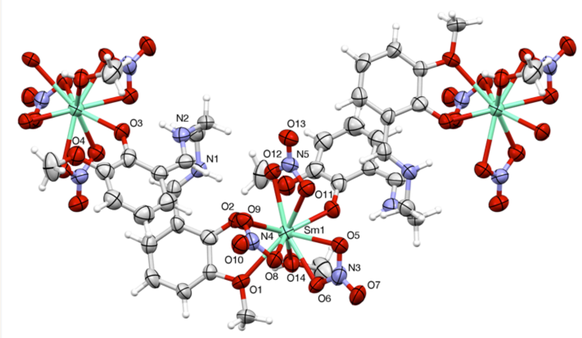
$[La(H_2L)(NO_3)_3]$ — monoclinic $P2_1/n$



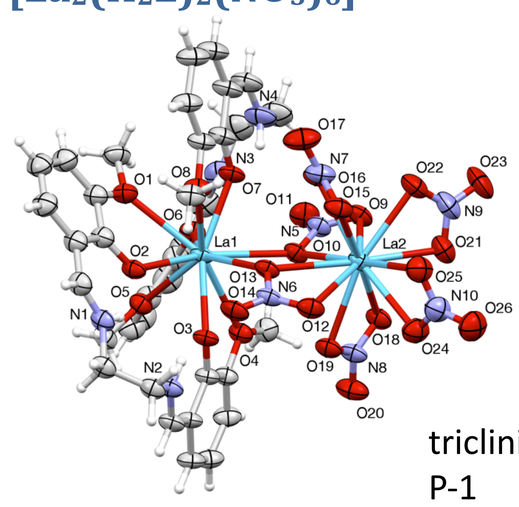
$[Pr(H_2L)(NO_3)_2(H_2O)_2]$ — monoclinic $P2_1/n$



$[Sm(H_2L)(NO_3)_3(MeOH)]$ — orthorhombic Pbca



$[La_2(H_2L)_2(NO_3)_6]$ — triclinic P-1



RNA cleavage ability

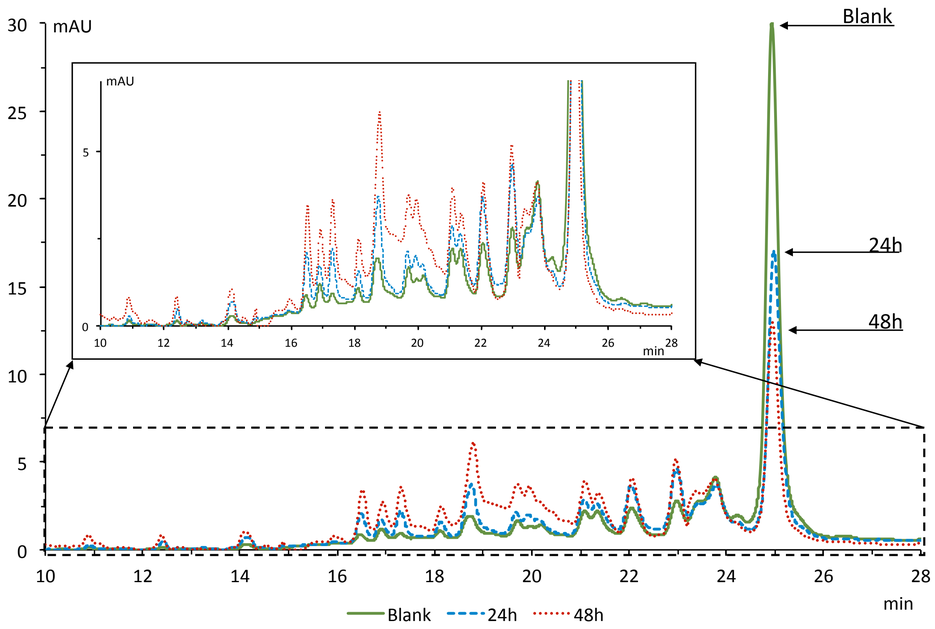


Fig. 1: *Cleavage of the 20-mer RNA oligonucleotide by the Pr^{3+} complex. Chromatogram overlay of the blank RNA oligonucleotide sample and its incubation at 24 h and 48 h with the complex is presented.*

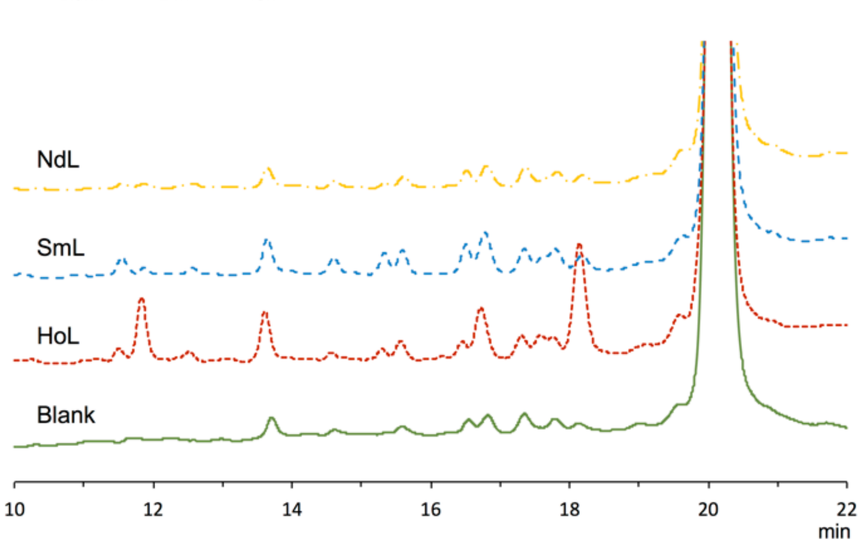


Fig. 2: *Cleavage of the 12-mer RNA oligonucleotide by the Nd^{3+}, Sm^{3+} and Ho^{3+} complexes. A chromatogram overlay of the blank RNA oligonucleotide sample and its incubation at 24 h with the complex is presented.*

NIR luminescence

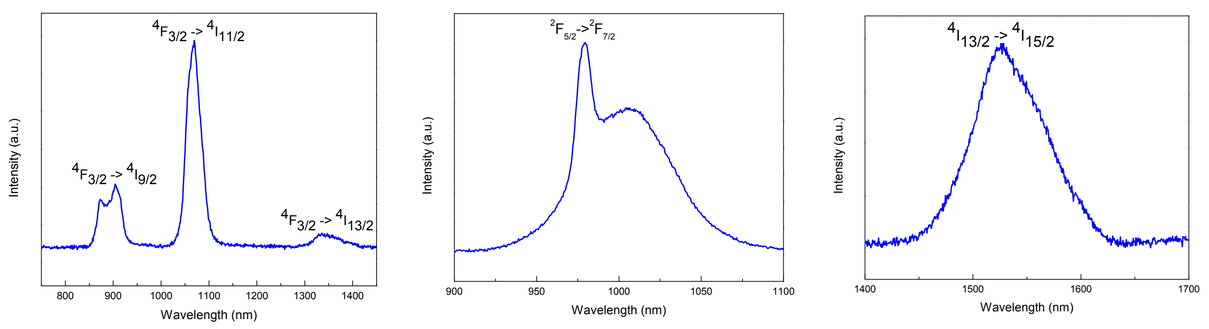


Fig. 3: *NIR Emission spectra of the (left to right) $Nd(H_2L)(NO_3)_3$, $Yb(H_2L)(NO_3)_3$ and $Er(H_2L)(NO_3)_3$ complexes (excited at 380.0 nm).*

Conclusion

Three unique crystal structures of La^{3+} and Pr^{3+} complexes, with the La^{3+} complex prepared in two different synthetic approaches, are reported, namely a dimeric $[La(H_2L)(NO_3)_3]_2$ complex, an asymmetric two-centered $[La_2(H_2L)_2(NO_3)_6]$ complex and a discrete mononuclear $[Pr(H_2L)(NO_3)_2(H_2O)_2]$ complex. For Nd^{3+} and Sm^{3+}, an isotypic mononuclear $[Nd(H_2L)(NO_3)_3]$ and 1D polymeric $[Sm(H_2L)(NO_3)_3(MeOH)]_n$ structure was obtained, respectively. The lanthanide complexes proved their capability to cleave a 20-mer RNA oligonucleotide 5'-AGC-GAU-AAG-AUU-CAU-AUA-UC-3' and a 12-mer 5'-GCA-CCC-UGU-CAG-3' in a non−sequence specific manner, demonstrating an interesting potential as valuable inorganic alternatives for the use of enzymes or ribozymes for RNA cleavage.

References

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2. J. R. Morrow, *Comment. Inorg. Chem.*, **2008**, 29, 169.
3. X. Yang, R. A. Jones, W.-K. Wong, *Dalton Trans.*, 2008, 1676.