The 21st International Electronic Conference on Synthetic Organic Chemistry

1-30 November 2017

# Synthesis of two asymmetric half-*salen* imine-type ligands as precursors of polynuclear metal complexes

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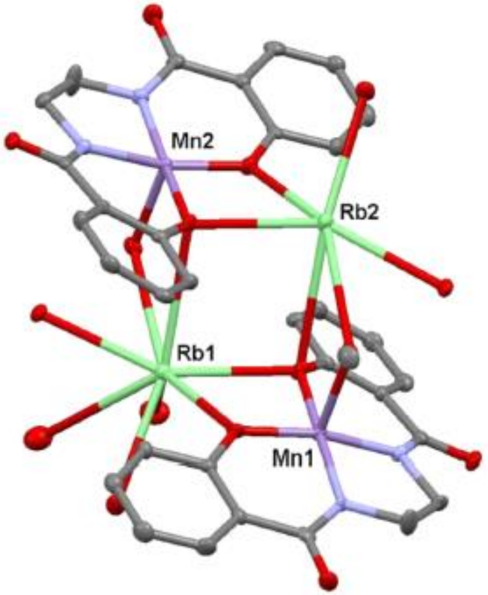
# Introduction

- Polydentate [N,O] ligands are considered as good candidates for the formation of polynuclear metal complexes with application as catalysts or models for mimicking the active sites in metalloenzymes.
- Our research group has employed *salen* or *half-salen* imine-type ligands to assemble polynuclear complexes that could be involved in catalytic processes or mimic the activity of the Photosystem II or catalase and peroxidase enzymes.

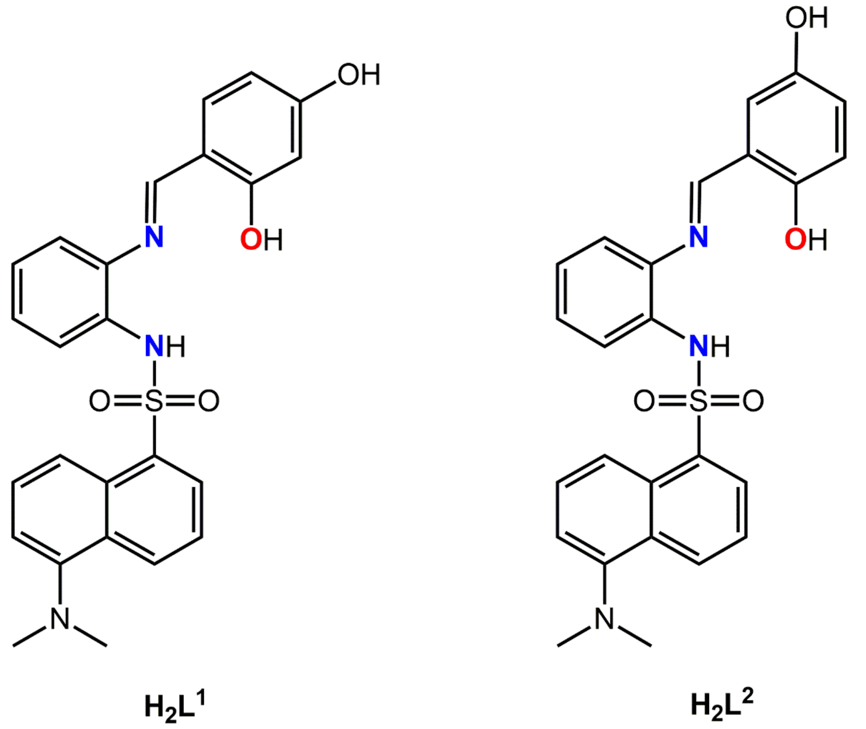


M. A. Vázquez-Fernández *et al*, *J. Inorg. Biochem.*, **2011**, *105*, 1538.

G. González-Riopedre *et al*, *Inorg. Chem.*, **2015**, *54*, 2512.

# Aims

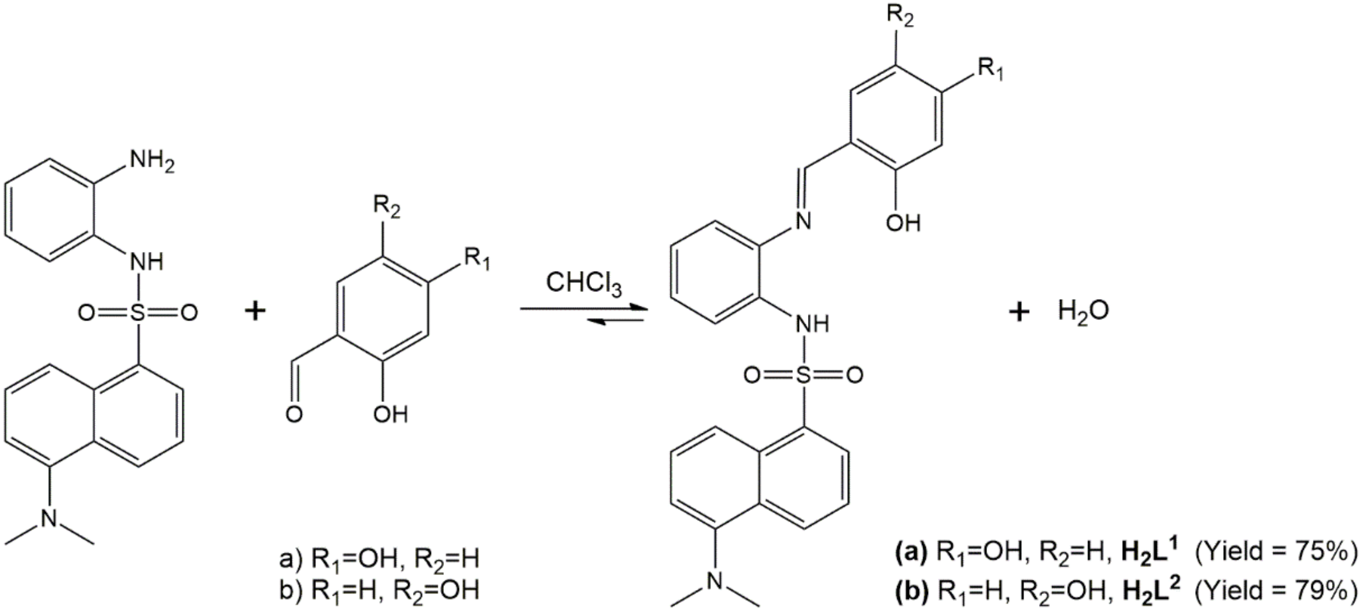
- ♣ Design and synthesis of two tridentate [NNO] half-*salen* ligands **$H_2L^1$** and **$H_2L^2$** (Scheme 1) bearing a further hydroxyl group as potential binding site.
- ♣ $H_2L^1$ and $H_2L^2$ can be suitable precursors for the formation of polynuclear supramolecular complexes.



**Scheme 1.** Imine-type tridentate ligands $H_2L^1$ and $H_2L^2$.

# Experimental

- Synthesis of two asymmetric Schiff base ligands (Scheme 2)
- Characterization techniques: E. A., ESI-MS, IR, $^1$H/COSY NMR, $^{13}$C/DEPT NMR



**Scheme 2.** Condensation reaction to obtain the tridentate ligands $H_2L^1$ and $H_2L^2$.

# Results

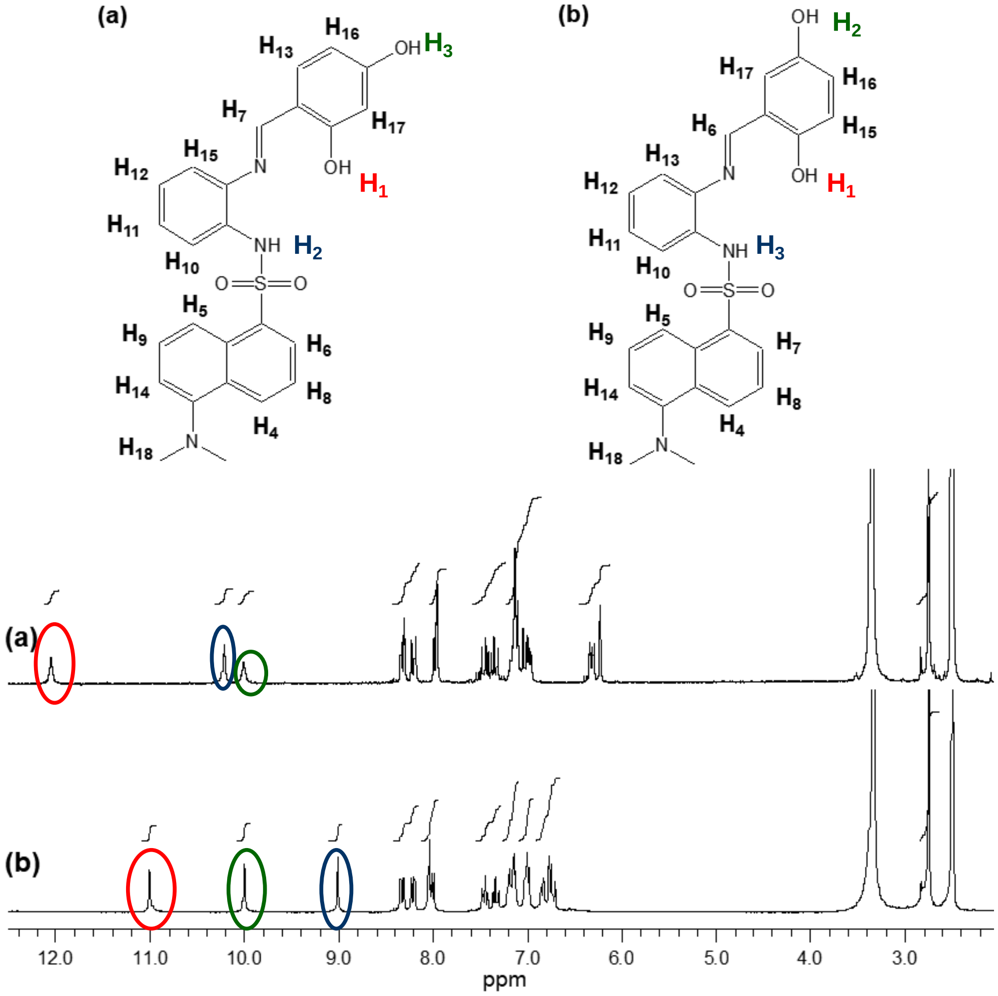


**Figure 1.** $^1$H-NMR spectra of $H_2L^1$ (a) and $H_2L^2$ (b) in DMSO-$d_6$.

## *Main differences:*

- The *para*-substituted ligand $H_2L^2$ has a lower melting point (ca. 90 $^{o}$C) than the *meta*-substituted ligand $H_2L^1$ (ca. 96 $^{o}$C).

- The salicylic OH (**$H_1$**) and the sulfonamide NH protons (in blue; Figure 1) in the *meta*-substituted ligand $H_2L^1$ **(a)** are more deshielded than those in the *para*-substituted ligand $H_2L^2$ **(b)**.

- Diverse metallosupramolecular structures might be obtained depending on several factors (e.g. nature of the metal ion, steric effects, acidity of the OH/NH protons, …).