

Justin Pothoof<sup>1</sup> / Michal Ruprecht<sup>1,2</sup> / Ben D. Sliwinski<sup>1,2</sup> / Ben M. Sosnowski<sup>1,2</sup> / Polly R. Fitzgerald<sup>1,2</sup> / Steven Kosmas<sup>2</sup> / Mark A. Benvenuto<sup>1</sup>

# Synthesis of “three-legged” tri-dentate podand ligands incorporating long-chain aliphatic moieties, for water remediators, and for isolating metal ions in non-aqueous solution

<sup>1</sup> Chemistry, University of Detroit Mercy, Detroit, Michigan, USA, E-mail: benvenma@udmercy.edu

<sup>2</sup> Grosse Pointe North High School, Grosse Pointe, Michigan, USA

## Abstract:

Two molecules, each including tris-2-amino-ethyleneamine (tren), have been produced using a Schiff's base condensation and long-chain, aliphatic aldehydes. The syntheses are straightforward and can be run in air at ambient temperature. The ability of these molecules to complex with metal ions makes them good candidates for water remediation. The ability of these ligands to hold metal ions in 0.03 M non-aqueous solutions was unexpected. Their syntheses and characterization are discussed.

**Keywords:** coordination chemistry, chelation, multi-dentate ligands, Schiff's Base condensation

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## 1 Introduction

### 1.1 The synthesis, chelators

The history of the production of multi-dentate ligands is approximately a century old, with salen having first been reported in 1933 [1]. Multi-dentate ligands can be produced in numerous ways, one of which is the addition of functional aldehydes to multi-amine molecules in what is the now classic Schiff's base condensation. The reaction is well-established, robust, and capable of being performed in virtually all solvents but water. The starting amine tren was used in this study precisely because it is stable, inexpensive, and easy to work with.

There are differences in how the Schiff's base condensation proceeds, according to whether or not the amine is aliphatic or aromatic. For example, aliphatic amines generally do not require elevated temperature for these condensations to occur, and can be run in most organic solvents. Aromatic amines normally do require elevated temperatures because of the stability of the benzene ring and its direct connection to the amine. This project used tren exclusively as the starting amine, an aliphatic amine, which meant that starting materials and reactions to form ligands could be handled easily and without elevated temperature.

Historically, people have almost always lived by water, and have always needed clean, potable water for their survival. This need has driven a number of different human innovations to clean or remediate saline, brackish, or otherwise polluted water – from evaporation, to settling and filtration through sand, to more specific and developed molecules for chelation [2–13]. Today, ethylenediamine tetraacetic acid has proven to be an excellent chelator, but this does not mean that the search for other molecules that can complex with metal ions in water is over [14–21].

Perhaps ironically, the presence of people near the very water that is needed for their survival and for an enhanced quality of life often means that water close to them becomes polluted through human activities. Examples of such activity include farming, mining, and large-scale transportation of commodities. For this reason and others, the search for effective means to clean water, and to do so in an economically favorable manner, is a continuing one.

Mark A. Benvenuto is the corresponding author.

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## 1.2 The pedagogy

This research is the result of a collaboration formed through the American Chemical Society's (ACS) Science Coaches Program, in which a high school teacher and high school students worked with a college professor and undergraduate college students. One of the authors (Kosmas) is a high school teacher, while another (Benvenuto) is a college professor. The ACS program encourages collaboration between the two levels of educator, but gives few guidelines about activities, other than urging them to be productive for students as well as teachers. This project became one in which four high school students and one undergraduate college student worked together to synthesize the target molecules.

It was felt that the project needed to be relevant to a modern problem – the cleaning of polluted water – and be based on techniques and processes that could be performed by a team that was both at the beginning of their careers as scientists and available to work in the laboratory for only limited amounts of time. Importantly, it was also a first step in expanding what can be called the green chemistry mindset of the researchers involved in it [22].

Importantly, these syntheses of new ligands for water remediation requires no more in terms of mathematical calculations than that which is seen in a general chemistry class, either at the high school or at the college level. A one-to-three stoichiometric ratio of amine to aldehyde can be used to produce the ligands. This is similar to any stoichiometry-based problem in a general chemistry class, simply using what might be described as more exotic chemical reagents than those that high school students normally see.

Another concept used and emphasized in the project is molarity, because it is easiest to use the target ligands as a solution of known concentration than it is to evaporate the solution to dryness, characterize the full sample, then measure small portions of the “dried” ligand for further use. This is because the target ligands, like many molecules which contain long-chain aliphatic moieties, exists as extremely viscous, waxy liquids. Thus, solutions of known concentration become a convenient way to deliver exact amounts of the ligands in reactions that formed metal–ligand complexes.

## 2 Safety

Tren and long-chain aliphatic aldehydes should be handled with care. In all cases in this study, students were supervised by faculty, although the actual reaction chemistry was always run by student researchers.

Likewise, perchlorate salts must be handled with care. In this study, all salts were purchased in small amounts (10 g bottles or smaller) to minimize any hazard should one be mishandled.

## 3 Discussion

### 3.1 Ligands

The ligand synthesis involves the addition of one molar equivalent of tren and three molar equivalents of octanal at room temperature, or three molar equivalents of dodecanal under similar conditions. The reaction was run in one of two solvents, monoglyme or toluene, and stirred mechanically for a minimum of 1 h, but can be stirred for days without degradation of the products. A solution of the starting amine in solvent is clear. Addition of the aldehyde produced pale yellow colors after stirring. Figure 1 shows an example of the reaction chemistry for the production of the ligand utilizing octanal, producing Ligand 1. If dodecanal is used, the three “arms” are simply four aliphatic carbon atoms longer (one *n*-butyl group longer per arm), resulting in Ligand 2.

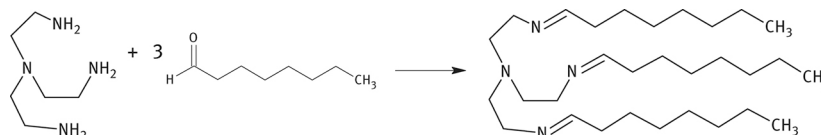


Figure 1: Representative ligand formation, Ligand 1.

### 3.2 Metal–ligand complex formation

The formation of ligand–metal complexes can occur through two different approaches. A solution of a metal salt can be produced in distilled water and added to a separatory funnel. The solution of the ligand is then

transferred into it in the separatory funnel and the two are mixed. Complex formation is immediate, and the complex precipitates into the aqueous phase. Alternatively, a sample of a dry metal salt can be added directly to the ligand in its non-aqueous solution. The complex can then be separated from the solution by rotary evaporation.

In this research project, emphasis was placed on being able to see the formation of a metal–ligand complex, as opposed to quantifying it through instrumental characterization techniques, such as  $^1\text{H}$  NMR. The reason is that the aim was to produce ligands and ligand–metal complexes in a manner that can be reproduced at the high school level. High schools do not normally have access to characterization techniques beyond UV-Vis spectrometers. Thus, characterization was confined to visible changes in solution colors.

The ability of an organic solution to hold metal ions in such a solution is not unheard of, but is relatively uncommon [23–27]. Since this occurred with seven of eight metals that were used to form complexes, the results of the complex formations through the direct addition of a dry salt to the ligand solution are summarized in Table 1. The transition metal ions were all delivered as perchlorate salts, while the lanthanide ions were all delivered as trifluoromethylsulfonate salts. It is noteworthy that the neodymium complex forms a precipitate at this concentration (0.03 M), while the other metal complexes do not do so.

**Table 1:** Metal complex relative solubilities.

Metal ion	Solubility at 0.03 M	Color
$\text{Co}^{2+}$	Soluble, no precipitate	Blue-green
$\text{Fe}^{3+}$	Soluble, no precipitate	Red-brown
$\text{Zn}^{2+}$	Soluble, no precipitate	Goldenrod
$\text{Cu}^{2+}$	Soluble, no precipitate	Green
$\text{Nd}^{3+}$	Precipitate forms	Yellow, with precipitate
$\text{Yb}^{3+}$	Soluble, no precipitate	Light yellow
$\text{Pr}^{3+}$	Soluble, no precipitate	Light yellow
$\text{Ho}^{3+}$	Soluble, no precipitate	Light yellow

## 4 Experimental

Reagents tris-2-aminoethylamine (tren) (98 %), octanal (99 %), and dodecanal (> 98 %) were purchased from Aldrich and used without further purification. Reagent purity was verified by running  $^1\text{H}$  NMR of a sample from each reagent bottle immediately upon opening. Solvents were also purchased and used without further purification.

All  $^1\text{H}$  NMR, of reagents as well as the target ligands, were run on a Jeol 300 MHz multi-nuclear instrument.

### 4.1 Ligand 1

The starting amine (0.25 g, 1.710 mmol) was added to a 60 mL of monoglyme or toluene and stirred for 5 min. No precipitate was present, and the resulting solution was a very pale yet transparent yellow. Three equivalents of octanal (0.690 g, 5.129 mmol) were then added and the resulting darker yellow solution was stirred for 16 h. The resulting 0.03 M solution was used for metal complexation trials.

### 4.2 Ligand 2

The starting amine (0.561 g, 3.84 mmol) was added to 100 mL of monoglyme (or 100 mL of toluene) and stirred. The resulting solution had a very pale white appearance. Three equivalents of dodecanal were added (2.121 g, 11.52 mmol) and the resulting solution stirred for 16 h. After stirring, the solution was a bright yet transparent yellow. This 0.038 M solution was used for metal complexation trials.

### 4.3 Complex formation

For Ligand 1, complexes of eight metal salts were formed. The  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$  were each added directly to Ligand 1 as perchlorate salts in a 1:2 molar ratio of metal to ligand. The  $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Ho}^{3+}$  were all added directly as trifluoromethylsulfonate salts.

For Ligand 2, only one complex was formed, using  $\text{Fe}^{3+}$ , added directly as a perchlorate salt, again in a 1:2 molar ratio of metal salt to ligand.

### 4.4 Control experiments

An aliquot of each unreacted ligand was placed in a sample vial of the same size as those in which the complexes were formed, and they were compared visually. In all cases, the starting ligand solution was not the same color as the complex solution.

In the case of Ligand 1 and the ytterbium trifluoromethylsulfonate, a one-half molar equivalent of the salt was added to a solution of just the starting amine in monoglyme, and the resulting solutions were visually compared. The amine–monoglyme–ytterbium salt solution was colorless, while the Ligand 1–monoglyme–ytterbium salt solution was a transparent yellow.

## 5 Conclusions and directions for the future

The search for effective, inexpensive molecules that can remediate polluted water is a continuing one. This research thrust has shown that there is a simple set of ligands that can be produced in a straightforward manner, at ambient temperature and pressure, and in a time frame that can be easily adapted to the time allotted to high school chemistry laboratory classes. This should be very easy to apply when teaching students in the upper levels of K-12 education, and should be amenable to performing research using local waters.

Importantly, this series of ligands appear to be a series of molecules that are able to function as water mediators. They readily complex with metal ions in water, and immediately form precipitates from aqueous solutions.

Additionally, the project emphasized a current problem that is direct and obvious, and with which high school and college students can easily identify.

It is believed that while this project gave satisfactory results, it might be expanded to determine if complexes form preferentially for specific Lewis acids, meaning larger versus smaller ions, or those with larger versus smaller charge-to-size ratios.

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