

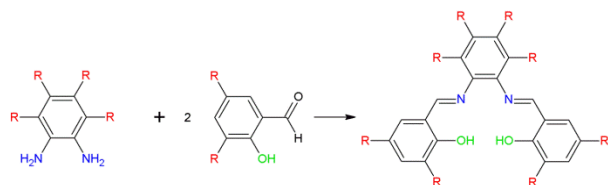
Synthesis and Characterization of Some Novel Tetradentate Schiff Base Ligands and their Metal(II) Complexes

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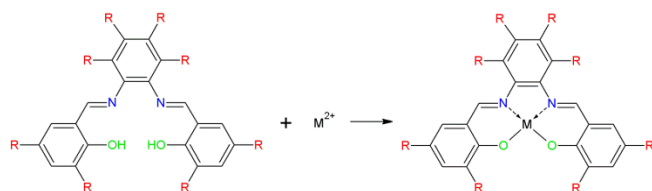
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Introduction

Schiff bases are functional groups derived from the condensation of amines and aldehydes, that is, the formation of carbon-nitrogen double bonds by interaction of amines and carbonyls. Incidentally, the Nitrogen acts as a ligand, or base, in which it readily donates an electron from its electron pair to a metal ion. The functionality of these ligands and their metal-complexes are the focus of much coordination and structural chemistry studies.^{1,2} These same studies lead to the observation of various properties that are luminescent,³ photochromic and thermochemical,^{4,5} and magnetic and electrochemical⁶⁻⁹ in nature. Furthermore, biological studies¹⁰ involve the many types of metal complexes afforded by such ligands and even provide antibacterial, or antimicrobial,¹¹⁻¹⁴ and antifungal¹⁵ properties. In many Schiff base studies, their effectiveness as catalysts is studied and utilized in many types of reactions.¹⁶⁻¹⁹ In the copolymerization of CO₂ with epoxides, a Co(II) complex of a Schiff base ligand facilitates the order and binding of CO₂ and epoxides, making it an effective catalyst.²⁰⁻²¹ Similarly, a Cu(II) complex of a Schiff base ligand was found to stabilize DNA for controlled binding of two separate DNA, acting as a scaffold to allow both structures to bind easily.²²



Scheme 1. The imines may be found in the ortho-position or, in this case, the meta-position. **R** denotes various halides and groups; the imines (**N-C**) and alcohols (**OH**) are coordination sites that give the ligand its tetradenticity.



Scheme 2. Metal coordination was performed on the meta-position diimines. The pair of electrons on the Nitrogen (**N**) and the unpaired electron on the Oxygen (**O**) coordinate to the metal(II) ion to form the complex.

The synthesis, characterization, and metal coordination of some novel and existing Schiff base ligands are studied in this project. Because there are various types of Schiff base ligands, those that will be studied are specified to symmetrical, tetradentate ligands: these are a 1:2 combination of a phenylenediamines and salicylaldehydes (**Scheme**

1). The term *-dentate* refer to the molecules ability to “bite down” onto metal ions; this is also known as *denticity*. Being *tetradentate* describes a number of *four* sites to which metal ions may attach to. Their metal complexes will involve metal(II) ions of copper, nickel, or zinc (**Scheme 2**). These metals are often coordinated to Schiff base ligands and have been studied together in a number of journals.²³⁻²⁵ Their data will aid in characterizing the metal complexes studied in this project by comparing this project’s data to existing ones

The synthetic process for Schiff bases, as described briefly, involves hours of condensation of two reagents: amines and aldehydes. This common synthetic method requires a solvent such as methanol or ethanol in which both reagents shall dissolve in, and a catalyst, usually an acid. Though simple and quite efficient, this method is sometimes modified or abandoned for more environmental and economic methods, such as those that do not require solvents.²⁶ For this project, the common synthetic method will not be employed. Instead, a more rapid and efficient method using copper nitrate catalyst without the need of reflux,²⁷ or condensation of reagents, is preferred.

Materials and Methods

All syntheses were carried out under a single fume hood. Reagents and solvents were not altered or purified in any way for use and were obtained mostly from Sigma-Aldrich. Instruments used for manipulation or analysis of product include a hydraulic pellet press, Fourier Transform Infrared (FT-IR) and Nuclear Magnetic Resonance (NMR) spectrometer, and later, X-ray Diffraction spectrometer.

General Synthesis of Schiff Base Ligands 1-7: Liquid salicylaldehydes were weighed into a 50 ml round bottom flask. (Salicylaldehyde has a density of 1.146 g/ml, meaning its measured weight shall deviate; additionally, this reagent will not act as the limiting reagent and the calculated amount *will* be increased by an additional 5% by mol.) 20-30 mL of ethanol is added to the salicylaldehydes to dissolve—some mixing, by addition of a stir bar and a stir plate may be necessary if the salicylaldehydes do not dissolve. In a 50 ml beaker, phenylenediamines were weighed out and dissolved in 10-20 ml ethanol. The solutions of phenylenediamines are added to the solution of salicylaldehydes slowly, via addition funnel. A small amount of copper nitrate (about 1 mol %) is added to the solution. It is then stirred for at least 30 minutes. The product is either filtered and

washed with cold ethanol or forced to precipitate with the addition of 50 ml of deionized water and later filtered. The product is air-dried and prepped for further analysis.

General Synthesis of Metal(II) Complexes 8-10: A reflux setup is required for the metal coordination reactions: a heating mantle, condenser, stir plate, and hoses, to allow water to cool the condenser, are necessary for the setup. Ligands were weighed onto a 50 ml round bottom flask. A 4:3 mix of methanol and chloroform is added to dissolve the ligand. This flask of solution is placed over a heating mantle and allowed to stir between 60-80°C for 5 minutes. Metal acetates are dissolved in methanol and added to the solution slowly. Afterwards, the solution is refluxed for a total of 3 hours. The end solutions may remain clear and are left in a refrigerator overnight (12-24 hours) to allow crystals to form. If no crystals form, the solution can be filtered or washed and air-dried.

Results and Conclusion

Dried samples of the Schiff base ligands and metal complexes were obtained. For ^1H and ^{13}C NMR experiments, the Schiff base ligands were dissolved in deuterated NMR solvents. Being deuterated gives the NMR solvents, such as chloroform, acetone, or dimethyl sulfoxide, hydrogen containing a pair of nuclei: both a proton and a neutron. Having a pair of nuclei will prevent the NMR instrument from detecting the single nuclei hydrogens as they will have no interaction with the magnetic field. The Schiff base ligand products were first dissolved in cheaper, non-deuterated solvents in order to find a proper NMR solvent for the NMR experiments. For ligands **1-7**, 5-20 mg of sample dissolved in 1 ml of their respective solvents.

The data obtained from ^1H NMR experiments display shifts of multiple hydrogens found on the molecule. These shifts are integrated and a reference shift—one that can be assigned to a particular proton on the molecule—is marked. By assigning the reference shift an integral number of 1 or the actual number of that hydrogen in one molecule, the integral values of the other shifts can be counted and matched with the actual amount of hydrogen found in one molecule. For ^{13}C NMR experiments, the unique carbon molecules on in the Schiff base ligands are observed (there are about 1% of ^{13}C in carbons found in nature, making them 'unique'). The number of shifts, their general shift values, and their heights give information about where and roughly how many carbon molecules are found in the sample.

In **Table 1**, a set of spectral data from some of the best data obtained are shown. The impurities and solvents are easily identified,²⁸ while the hydrogen integral values and number of unique

carbons aid in identifying the existence of the synthesized Schiff base ligands.

Table 1. NMR Spectral Data

1 (CDCl_3)	4 (CDCl_3)	2 ($(\text{CD}_3)_2\text{CO}$)
^1H (ppm)		
8.66 (s, 2H)	12.36 (s, 1H) ^b	12.39 (s, 1H) ^b
7.31-7.49 (m, 6H)	8.72 (s, 2H)	8.85 (s, 2H)
7.12-7.22 (m, 2H)	7.99-8.07 (m, 4H)	7.61-7.65 (d, 2H)
6.90-7.10 (m, 4H)	7.46-7.48 (m, 4H)	7.42-7.48 (m, 2H)
2.15 (s) ^a	7.25 (d, 1H)	7.22-7.26 (d, 1H)
	7.03 (m, 4H)	7.08-7.13 (d, 2H)
	6.76 (m, 2H)	6.95-7.04 (m, 3H)
	4.74 (s, 3H) ^c	4.85 (s) ^c
	1.56 (s) ^d	2.08 (s) ^f
	1.25 (s) ^e	2.04 (q) ^g
^{13}C (ppm)		
163.44	164.78	165.35
161.27	160.87	160.96
149.82	146.96	133.75
133.55	139.32	133.27
132.56	134.29	119.58
130.41	133.04	119.35
119.70	124.49	117.07
119.29	119.87	116.86
119.17	119.10	105.83
117.42	117.37	105.59
114.04	114.81	153.50
	113.83	155.80

^aacetone ^b ^2H expected—possible deuteration ^camine from phenylenediamine impurities—this affects **4** by having too many H in the aromatic region ^dwater ^eethanol ^f ^{18}O solvent/acetone

Table 2. IR Bands (cm^{-1})

Cmpds	$\text{V}_{\text{O-H}}$	$\text{V}_{\text{C=N}}$	$\text{V}_{\text{C-O}}$	$\text{V}_{\text{N-M}}$	$\text{V}_{\text{O-M}}$
Ligand 2	3385	1566	1119	-	-
Cu(II)	-	1594	1107	546	502
Ni(II)	-	1606	1136	530	503
Zn(II)	-	1591	1148	522	469

The IR Data obtained gives information on the existence of specific bonds found in the ligands and metal complexes. The bonds in the molecules have different modes of vibration that the FTIR instrument detects and displays in a spectra form. These bonds are consistent in many molecules, so that identifying the presence of the bonds by comparing with known values is done. To determine that the Schiff base ligand **2** was metal-coordinated, the metal-oxygen and metal-nitrogen bonds were found on the spectra and compared with the values of spectra reported in journals.²⁹⁻³⁰ The values of these bonds were consistent, giving some proof that the Schiff base ligand had been metal-coordinated. **Table 2** displays some of the shifts in the spectra.

By employing an alternative method to synthesize Schiff base ligands, a novel Schiff base ligand was found. And due to the ability of a ligand to bind to metals, additional three metal complexes were synthesized. The use of powerful instruments, like the NMR and FTIR, provided characterization to confirm the presence of the target ligands and complexes. In the future, these compounds should yield crystals to allow X-ray crystallography experiments to determine fully, the molecular details of the compounds.

The search for a novel ligand has been successful in this project and will continue, given the variety of Schiff base ligands that have not yet been synthesized. Studies on the properties of these novel ligands will also produce interest in other fields of chemistry and science, as a result of numerous properties displayed by many Schiff base ligands. In the future, more metal complexes may be synthesized and characterized. Other methods that may yield a higher percentage of products can also be useful, and a process to do so can be studied and found. Future work may include studying the synthesis of Schiff base ligands and their metal complex, so that a better or more efficient and novel method may be utilized. This type of study will involve different types of experiments and additional sets of instruments. This project would aid in the overall study of the Schiff base ligands, their metal complexes, and synthetic chemistry, as a whole.

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