

Ft-Nmr Spectroscopy in Schiff Bases: Synthesis, Applications, and Characterization

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ABSTRACT

A class of chemicals known as Schiff bases are created when primary amines condense with carbonyl compounds. They contain imine (-C=N-) functional groups, which have various uses in industry, medicine, and catalysis and serve as ligands in coordination compounds. Using m-nitrobenzaldehyde and p-chloroaniline, Schiff base compounds were produced in an experimental work. The Schiff base's nitro group was later converted into an amino group via reduction. Both the 4-Chloro-N-[(E)-(nitrophenyl)methylene]aniline and 4-Chloro-N-[(E)-(aminophenyl)methylene]aniline that were produced with this process were successfully synthesized. They followed the successful characterization of the synthesized Schiff base compound and the reduced Schiff base compound using FT-NMR and additional characteristics like melting point, color, nature, etc. This study was conducted with several applications for Schiff base compounds in mind.

Keywords: Synthesis and characterization, coordination chemistry, FT-NMR, ligands, and Schiff bases.

INTRODUCTION

Schiff bases are imine or azomethine groups with the formula (-C=N-). Condensation between primary amines and carbonyl compounds produces Schiff bases. Hugo Schiff first reported these compounds, hence the term "Schaffer base."

There are numerous uses for Schiff-based chemicals in the chemical and pharmaceutical sectors. These substances display a variety of biological behaviors. It includes antibacterial, antidyslipidemic, antitubercular, antihelminthic, anticonvulsant, anti-inflammatory, antiviral, and antioxidant properties, among other things.

In addition to having therapeutic benefits, Schiff base molecules are essential ligands in coordination chemistry. They typically consist of polydentate ligands with nitrogen and oxygen donor atoms that are macrocyclic or macrocyclic.

Schiff bases may have potential qualities, including magnetic properties, biological traits, coordination ability, and medicinal benefits. They serve as a route for synthesizing many molecules with carbon-nitrogen linkages.

This study synthesizes a Schiff base molecule through the condensation reaction between an amine and a carbonyl compound. With the aid of p-chloroaniline and m-nitrobenzaldehyde, the Schiff base 4-Chloro-N-[(E)(nitrophenyl)methylene] aniline was created. The base's nitro group was then converted into an amino group, leading to the synthesis of 4-Chloro-N-[(E)-(aminophenyl)methylene] aniline.

A light-yellow organochlorine chemical called 4-chloroaniline (C₆H₄NH₂) is also known as p-chloroaniline. A nitro group has been meta-substituted to an aldehyde in the organic aromatic molecule 3nitrobenzaldehyde/m-nitrobenzaldehyde. The FT-NMR instrumentation was used to characterize the produced chemicals. The peak for amino group protons and the proton bound to the imine linkage were recorded.

METHODOLOGY

This research study's goal was to synthesize and characterize Schiff base compounds while considering the numerous uses that these compounds can be put to.

The following were the study's key takeaways.

1. P-chloroaniline and m-nitrobenzaldehyde are used in the synthesis of a Schiff base.
2. Sn/HCl is used as the reagent in reducing the nitro group into an amino group.
3. Characterization of the produced Schiff base compound and the reduced compound using FT-NMR and other physical indicators such as color change, physical nature, and different melting points for reactant and product.

MATERIALS EMPLOYED

1. Nuclear magnetic resonance (NMR) spectrometer made by Bruker, 400 MHz.
2. Accessories and a mantle for heating.
3. Flask with a circular bottom and other glass items.
4. M-nitrobenzaldehyde, p-chloroaniline, tin, glacial acetic acid, and hydrochloric acid are among the chemicals.

THE SCHIFF BASE IS CREATED THROUGH A CONDENSATION REACTION BETWEEN M-NITROBENZALDEHYDE AND P-CHLOROANILINE.

The procedure entails refluxing a second mixture of mNitrobenzaldehyde and p-Chloroaniline separately dissolved in ethanol and taken in a flask with a flat bottom.

One or two drops of the catalyst, glacial acetic acid, are added to the flask during refluxing. A solid precipitate is created during refluxing. The Schiff base is the result.

The mixture in a round-bottomed flask had a light yellowish hue before the condensation reaction, which resulted in a deeper yellowish cream, both before and after the reaction, a hue shift was seen.

BEFORE REPLACING AFTER REFLUCING



The condensation reaction's outcome

The reaction state was kept such that cooling began after the flask lost heat. The flask was allowed to partially cool before being artificially cooled. It was discovered that the product had a yield of about 60%.

The melting point of the substance was discovered to be around 84oC. The reactants' melting temperatures for p-chloroaniline and m-Nitrobenzaldehyde were 58.5°C and 72.5°C.

REDUCTION OF THE SCHIFF BASE COMPOUND

A Schiff base was the end product of the reaction after the reactants were condensed. The m-Nitrobenzaldehyde's NO₂ group was then decreased from this product to give it an NH₂ group. The Sn/HCl reagent was used to perform the reduction.

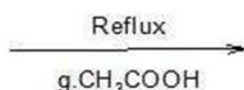
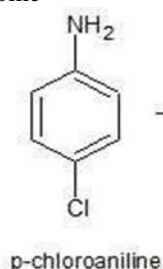
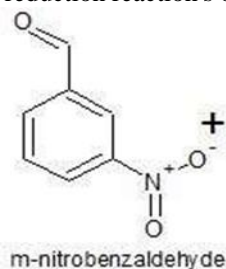
The slightly heated HCl solution receives tin. Additionally, the reducing agent-containing solution received the condensation product, which was then given time to precipitate. It was discovered that the color of the newly produced product was different from the color of the condensation product. It went from being a creamier yellow hue to a darker brown hue. The product had a yield of about 60%.

It was also discovered that the final product's melting point differed from the original. It was found to be 75°C instead of 84°C for the older product.

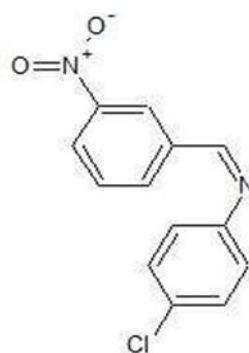


PRIOR TO REDUCTION

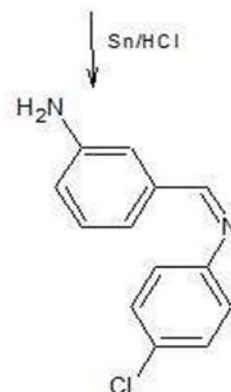
A reduction reaction's outcome



BEFORE REDUCTION



4-Chloro-N-[(E)-(3-nitrophenyl)methylene]aniline



4-Chloro-N-[(E)-(3-aminophenyl)methylene]aniline

A diagrammatic depiction of the test

Determine the solubility

In methanol, both produced products could be dissolved.

Check for aromatic amines

To determine whether aromatic amine was present, an azo-dye test was used. The reaction of the reduced Schiff base product with nitrous acid produced an orange-colored dye. When -naphthol was introduced, it generated diazonium salts, which underwent a coupling process.

FT-NMR analysis

The Schiff base compound and the reduced compound underwent FT-NMR investigation. The characterization was finished after recording the protons' peaks.

RESULT AND CONVERSATION

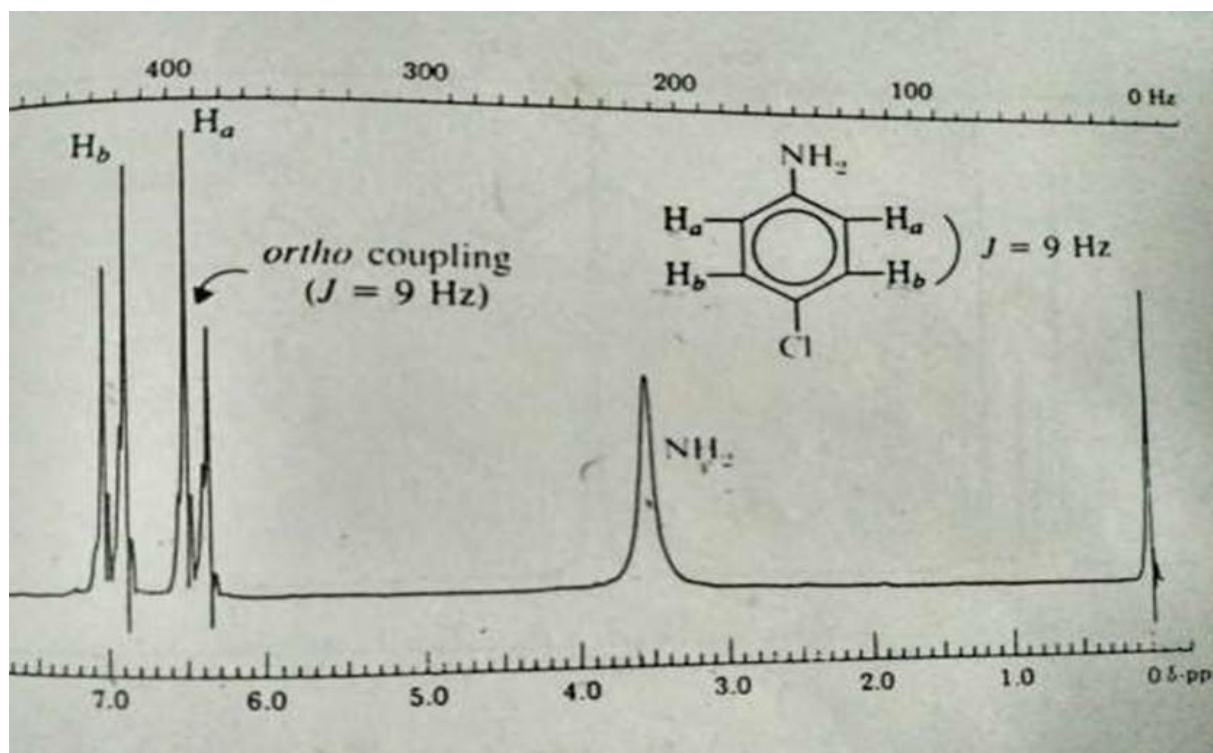
Table 1: Physical traits of the reactants and products.

Sample	Melting Point	Colour	Physical appearance
m-Nitrobenzaldehyde	58.5 °C	Brownish	Crystalline
p-Chloroaniline	72.5 °C	Pale yellow	Crystalline
4-Chloro-N-[(E)-(nitrophenyl)methylene]aniline	84 °C	Creamy Yellow	Crystalline
4-Chloro-N-[(E)-(aminophenyl)methylene]aniline	75 °C	Brownish	Crystalline to granular

The table demonstrates how the items' colors and melting points differ. It means that a distinct chemical from the reagents was created.

FT-NMR EVALUATION

The synthesized materials' NMR spectra showed the following distinctive characteristics. For p-chloroaniline.

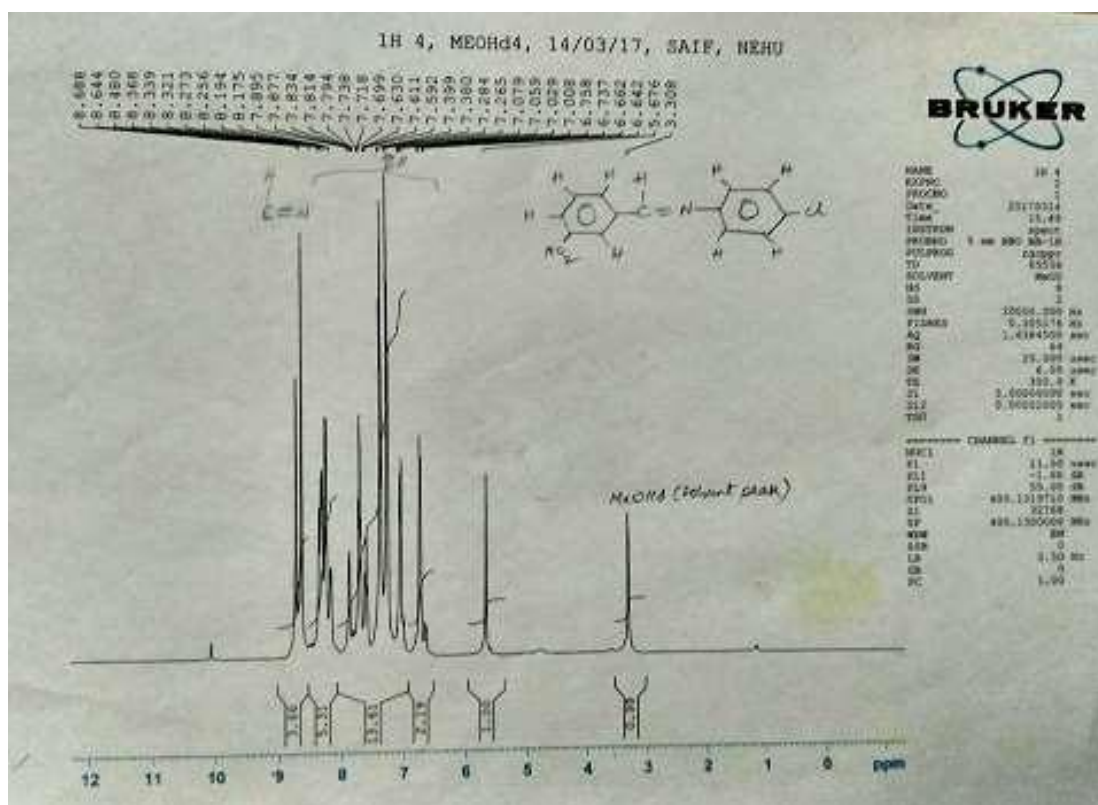
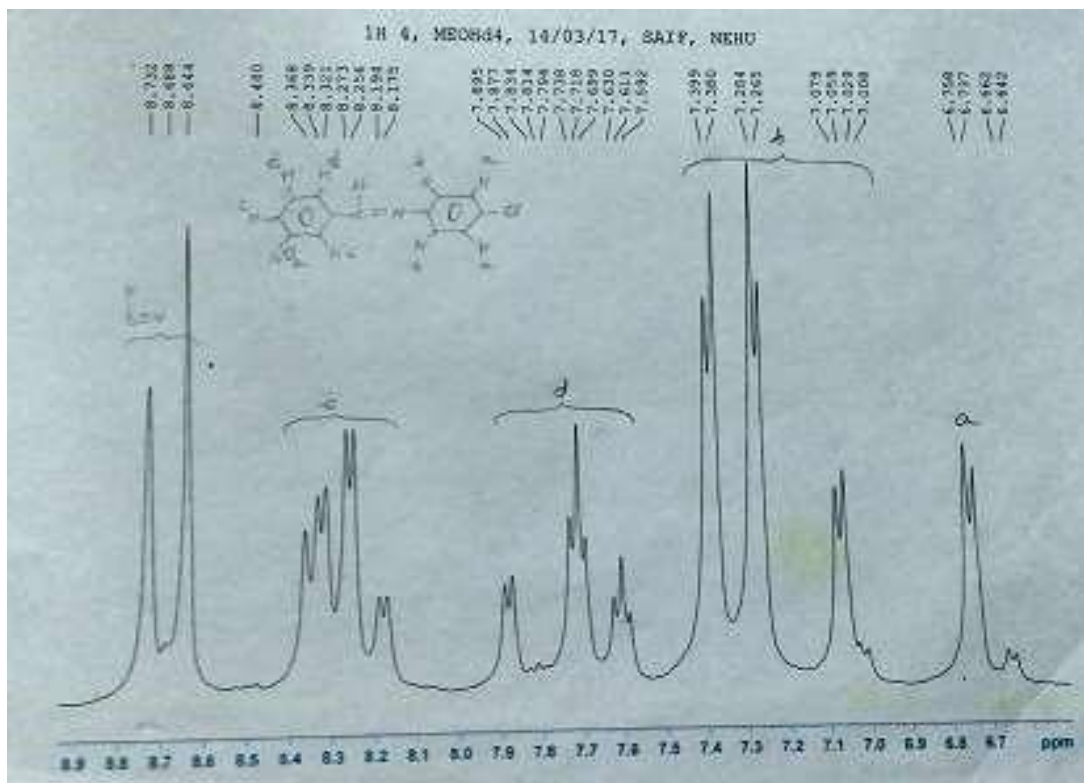


Substituents frequently cause chemical changes that are large enough to display first-order spectra. This is true for benzene derivatives containing electron-donating (shielding) and electron-withdrawing (de-shielding) groups. The benzenoid hydrogens can be seen as a set of two doublets in the NMR spectra of p-chloroaniline. The two hydrogens have a 9Hz coupling constant, typical for ortho coupling. The pairings Ha and Hb are chemically comparable in p-chloroaniline and related systems but are not magnetically equivalent.

THE SCHIFF BASE COMPOUND'S NMR SPECTRA

The signal for the deuterated methanol solvent may be found in the singlet peak at 3.308 ppm. The proton present in the CH=N group has a peak that ranges in intensity from 8.644 to 8.732 ppm in the duplet spectrum.

Protons have a peak represented by the letter "c" in the above diagram, ranging from 8.175 to 8.368 ppm. The protons nearby are affected because NO₂ is an electron-withdrawing group. They lose density and exhibit downfield chemical shifts as a result. Protons with type designations have maxima in the 7.592 to 7.895 ppm range. The 'b' protons range from 7.008 to 7.399 ppm.

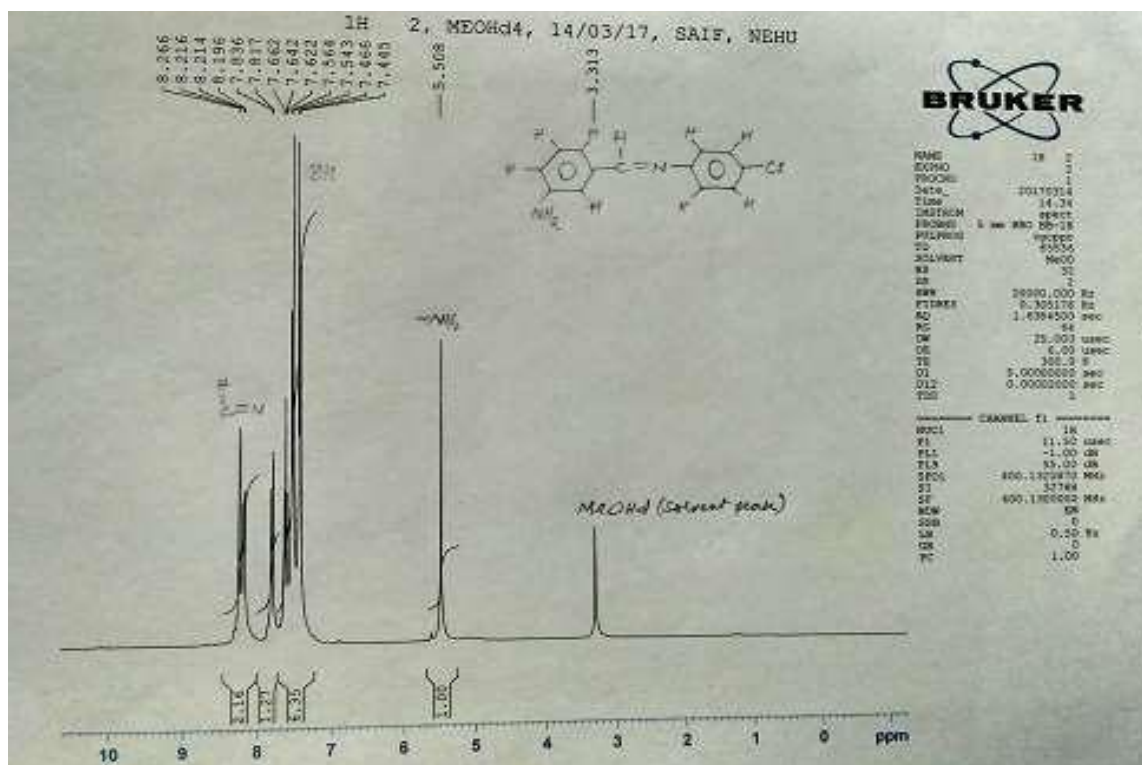
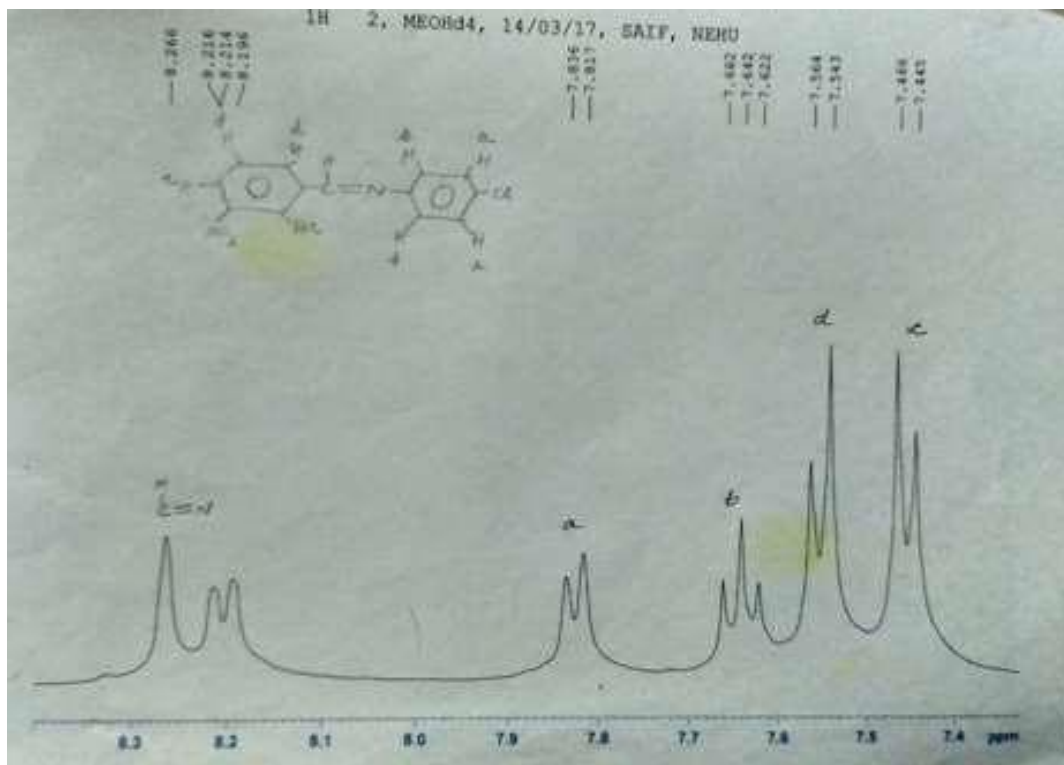


The 'a'-designated protons have a mass between 6.642 and 6.758 ppm. Because the Cl group is extremely electronegative in this situation, it withdraws charge, which causes the electron density to drop and causes a downfield chemical shift. The protons near NO₂ resonate at a lower field than the protons near Cl because NO₂, which is more electronegative than Cl, can attract electrons more remarkably.

THE REDUCED COMPOUND'S NMR SPECTRUM

The solvent employed, deuterated methanol, is revealed by the singlet peak at 3.313 ppm. The peak for NH₂ is the singlet peak at 5.508 ppm. The proton of the CH=N group exhibits a triplet peak between 8.196 and 8.266 ppm.

“ protons have a mass between 7.817 and 7.863 ppm, while 'B' protons have a mass between 7.622 and 7.662 ppm.



The range of 'd' and 'c' protons is 7.543 to 7.564 ppm, and the range of 'c' protons is 7.445 to 7.466 ppm. In this case, in contrast to the preceding Schiff base data, the NH₂ group's electron release raises the electron density of the nearby protons, shielding the nucleus and causing resonance upfield. Thus, the protons symbolized by the letters "c" and "d" are in the upfield as opposed to the protons denoted by the letters "a" and "b," which are close to the electron-withdrawing group Cl and experience a downfield chemical shift.

CONCLUSION

Numerous fields benefit from Schiff base compounds. They can be produced synthetically and used as ligands or in conjunction with other chemicals for medicinal purposes. A Schiff base compound and a reduced Schiff base compound are synthesized and described in this experimental research work.

The Schiff base chemical 4-Chloro-N-[(E)-(nitrophenyl) methylene] aniline was created via the condensation of m-Nitrobenzaldehyde and p-Chloroaniline, which was then reduced to 4-Chloro-N-[(E) (aminophenyl) methylene] aniline. Simple and inexpensive methods have been used to create the targeted chemicals.

FT-NMR Spectroscopy is used to characterize these two substances. Between 8.644 ppm and 8.732 ppm, the spectrum of the proton bound to the imine linkage of the Schiff base peaks out. At 5.508 ppm, the highest resonance of the amino group protons occurs.

Characterization also considers particular physical criteria like color change, physical nature, and the difference between reactant and product melting temperatures.

There is room for more investigation. The Schiff base compounds can function as ligands, and central metal atoms can be used to create coordination complexes. As a result, Schiff base-derived ligands will be formed. Burns et al. and MacLachlan et al.'s study, which describes Schiff base-derived ligands with a nitrogen or oxygen donor group, supports this. Additionally, nitrogen and oxygen donor groups are present in the molecules that this study produced.

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