Remittances Review
September 2024,
Volume: 9, No: S 4, pp. 724-732
ISSN: 2059-6588(Print) | ISSN 2059-6596(Online)
Received : 20 July 2024, Accepted: 25 September 2024
DOI: https://doi.org/10.33282/rr.vx9i2.41

REFLUX SYNTHESIS AND CRYSTALLOGRAPHIC STUDIES OF N, N-(1,2-PHENYLENE) DIPROPIONAMIDE AND ITS METAL COMPLEXES

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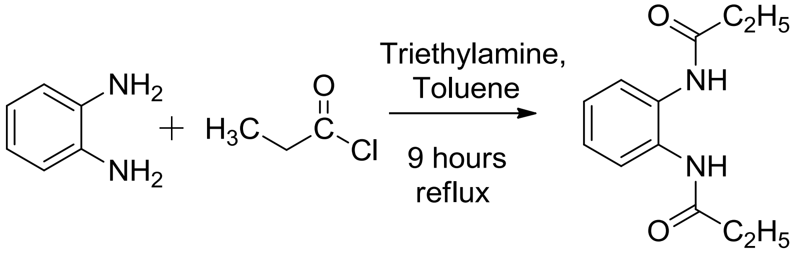
Abstract

N, N-(1,2 –Phenylene) dipropionamide was prepared by the reaction of propionyl chloride 6ml, orthophenylene diamine (3g) and triethylamine (6ml) in 100ml of anhydrous toluene. This reaction was refluxed for 16 hours and then allows to stand at room temperature. The temperature was maintained at 110C. Once the temperature of the solvent maintained, the reaction become started. The crude product has been crystallized with ethanol. Brown solid crystals were obtained with 49% yield having melting point 322.71°C. Different metal ligand complexes were prepared with the synthesized ligand. Ligand and complexes were analyzed by using different characterization techniques including X-ray diffraction, FTIR.



Keywords

N, N-(1,2-Phenylene) Dipropionamide, Propionyl Chloride, Orthophenylene Diamine, Triethylamine, Crystallization, Brown Crystals, Metal Ligand Complexes

INTRODUCTION

An organometallic compound is one that has metal carbon link in its structure. In many organometallic compounds both sigma and pi bonding exist between metal atom and carbon. Type and character of organometallic compound can behave as ionic, covalent or in-between. Organometallic complexes are those in which a metal and organic ligands form dative covalent connections. In recent year medicinal organometallic chemistry research has mostly worked on the synthesis of organometallic compounds for anti-cancer anti-malarial applications. Organometallic compounds and their physiochemical characteristics are normally utilized in homogenous catalysis (Bilal[a,b], 202). They are attractive therapeutic candidates for cancer treatment because of their structural variety, ligand exchange and catalytic characteristic. Metallocenes, metal-arenes and metal-carbene ligands are showing greater use in medical organometallic chemistry.

Amides are commonly known as carboxamide created by derivatives of carboxylic acid and ammonia molecules. Amide is a group which is little bit less rigid than imide group. Amide is a nitrogen containing group that belongs to one of two classes'' ammonia and amines''. Covalent amides are compounds that are neutral or weakly acidic than the hydroxyl group (OH) of an acid is replaced by an amino group (NR_2), in which R may represent a hydrogen atom or an organic combining group such as methyl group CH_3. The most important group is carboxamide (R'COOH). Amides (those that include at least one –NH bond) have extremely high melting and boiling points. They are soluble in water due to their ability to form hydrogen bonds. Amides are less reactive than amines but more reactive than esters, carboxylic acids, ketones and aldehydes (Bilal[a,b] et al., 2024). Amides in water do not display noticeable acid base characteristics because of amine's CO electrophilic effect. Amides have a CO band of moderate strength about 1650cm^{-1}.CONHR signals have been found in the H-NMR low field area. In X-ray crystallography, the –CON center and neighboring atoms contribute considerably to the formation of a plane. As a result, the amide linkage is planar (Sattar et al., 2024).

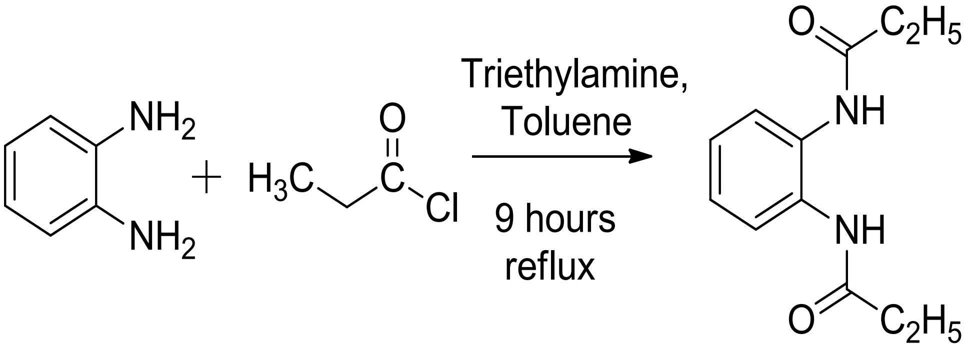
Amides are extensively used for catalytic, anti-bacterial, anti-oxidant and other biological activities. Amides constantly attract much interest because of their distinct and vast applications (Basharat et al., 2024). Piperazine diacetamide ligand show biological activity with cobalt zinc and complexes. Piperazine ring base substances are used in anti-bacterial activity. Ferroquine is most widely used as chloroquine derivative having anti-malarial activity. Ferroquine and its derivatives have showed great capability as clinically relevant anti-malarial. Schiff base ligand (N-[4-(Phenyliminomethyl) phenyl] acetamide) and its cobalt and nickel complexes have showed anti-bacterial activity. Cisplatine, carboplatin and oxaliplatin are metal complexes with platinium centeral atoms have a significant influence on modern cancer treatment. Cisplatin has become one of the most commonly used medicine and is a very successful in treating a variety of malignancies including ovarian and testicular tumors.

MATERIALS AND METHODS

Ortho phenylenediamine with molecular weight 108.144 used 3g (0.02moles). Propional chloride with molecular weight 92.52 used 6ml (0.06moles). Triethylamine with molecular weight 101.193 used 6ml (0.04moles).

Procedure

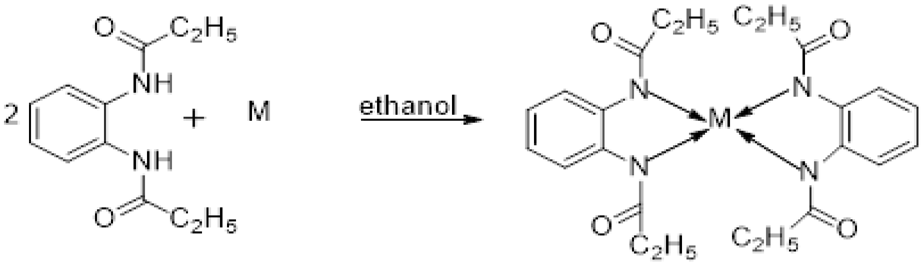
Ligand was synthesized by the mixture of propionyl chloride (6ml) with O-phenylenediamine (3g) and triethylamine (6ml) in 100ml anhydrous toluene. This mixture was refluxed in two neck round bottom flask about 9 hours in inert condition. The flask was placed on oil bath with continuous stirring of solution. The reaction mixture was placed on the hot plate and the temperature was maintained at 110°C. Once the temperature of the solvent has been maintained, a reaction started. Color changing of the reaction mixture was noted after 9 hours, which indicated that reaction was completed. After filtering the reaction mixture, the filtrate was received in a beaker and crystals formed. The crude product has been recrystallized with ethanol. TLC at different stages with different ratios (n-hexane: THF 1:4) was carried out. The melting point of crystals is 160°C and we get the proportion yield which is 49%.



Scheme: Synthesis of ligand N, N (1, 2-phenylene) dipropionamide)

Synthesis of tin-ligand complex 1

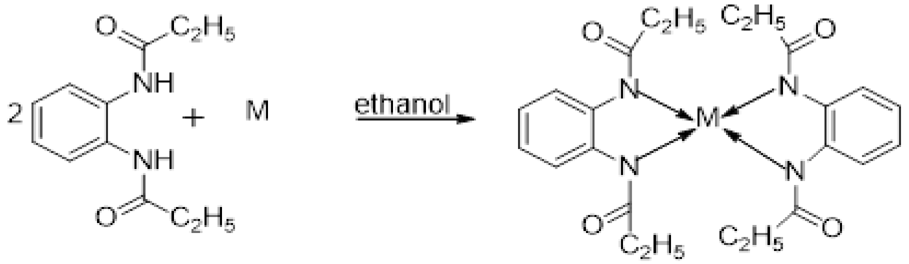
Metal ligand complex was synthesized by the way of aggregate of ligand N, N (1, 2-phenylene) dipropionamide) 0.55g with the metallic salt (stannous chloride) 0.547g in 50ml ethanol in a neck round bottom flask for three hours refluxed with nonstop stirring of solution. After three hours the reaction was completed and TLC at different stages with different ratios were carried out. A clear single spot appeared at TLC card.



M= Sn

Synthesis of sodium-ligand compound 2

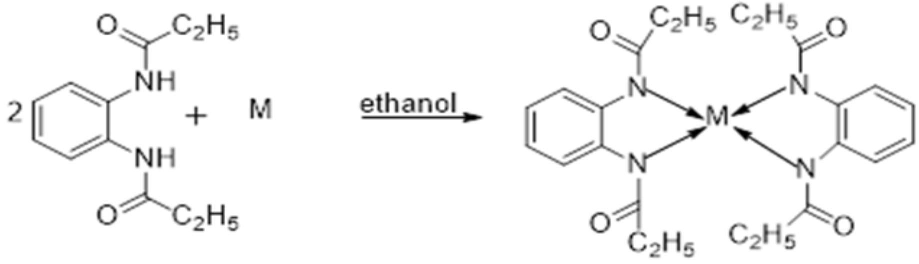
Ligand–metal compound was synthesized by using (1.1g) with alkali metal salt (sodium acetate) (0.68g) in 50mL ethanol in a neck round bottom flask for 3 hours with non-stop stirring of solution. Then the TLC at different stages has been performed with different ratios: a clean single spot appeared at the TLC card. Now pour the reaction mixture from the flask in beaker. Evaporation of reaction mixture was done by rotary evaporator. Then cover the mixture with aluminum foil and rest it till the crystals formed.



M = CH_3COONa

Synthesis of zinc-ligand complex 3

0.1M (0.3g) of N, N (1, 2-phenylene)dipropionamide) and 0.05M (0.13) of ZnCl2 in 50ml of ethanol were combined in a 250ml round-bottom flask and stirred at room temperature for 3 hours. TLC was used to monitor the completion of the reaction using n-hexane and tetrahydrofuran (1:4). The resulting brown colored reaction mixture was concentrated using a rotary evaporator and allowed to recrystallize.



M=Zn

Synthesis of nickelocene 4

Nickelocene was Synthesized by reaction of benzene (1.6ml) with a metallic salt (nickel chloride hexahydrate) (2.4g) in 100mL ethanol in a neck round bottom flask for 3 hours with non-stop stirring. Then it was refluxed for 1hour, the reaction was completed, and TLC was performed at several stages with varying ratios of solvent system a clear single spot on the TLC card was appeared. Then solvent was evaporated by using rotary evaporator. After that, filtrate was covered with aluminium foil and let it lie to form crystals.

RESULTS AND DISCUSSIONS

Ligand product is obtained with 49% yield and melting point noted at 322.71°C. Genesis of product is validated through spectrographic approaches. Diffracting procedures by utilizing x-rays confirmed the crystalline structure of ligand and respective complexes. The powder XRD is used to figure out how crystalline substances are made. According to the PXRD results, the ligand has a tetragonal shape. In complex 1, the disappearance of an absorption peak at 3798cm^{-1} for the –N-H group and the appearance of an absorption peak at 1010.80cm^{-1} corresponding to the stretching vibration of the resulting N-Sn bond confirms the formation of Sn(II) complex of N,N’(1,2-phenylene) dipropionamide. In compound 2, appearance of an absorption peak at 490 cm^{-1} corresponding to the stretching vibration of the resulting N-Na bond which confirms the formation of Na compound of N, N (1, 2-phenylene)dipropionamide. In complex 3, the disappearance of an absorption peak at 3798 cm^{-1} for the –N-H group and the appearance of an absorption peak at 452 cm^{-1} corresponding to the stretching vibration of the resulting N-Zn bond confirms the formation of Zn(II) complex of N,N’-(1,2-phenylene)dipropionamide.In complex 4, absorption peak at 435 estimated formations of Nickelocene.

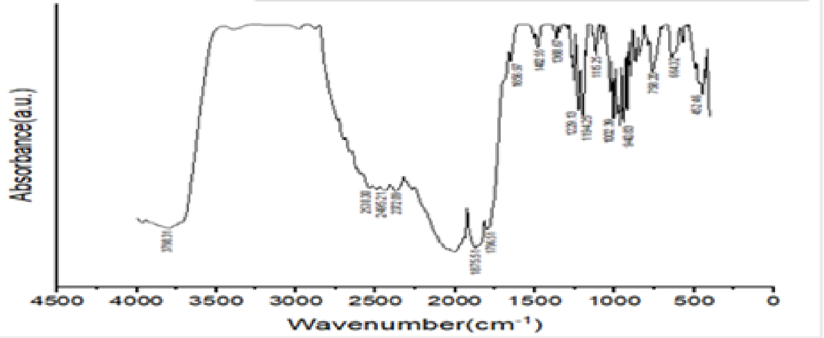


Figure 1: FTIR spectra of ligand N, N (1, 2-phenylene)dipropionamide

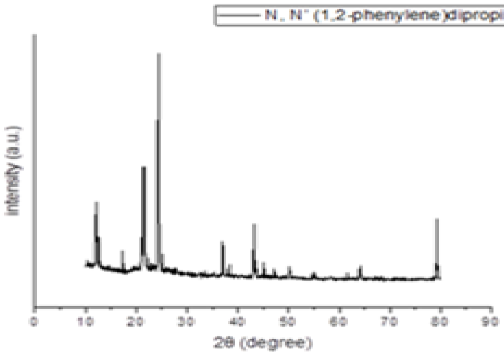


Figure 2: XRD spectra of ligand N, N (1, 2-phenylene)dipropionamide

Table 1: Chemicals for synthesis of ligand N, N (1, 2-phenylene)dipropionamide

Reactants	Molecular weight	Quantity	Moles
O-phenylenediamine	108.144g	3g	0.02
Propionyl chloride	92.52	6mL	0.06
Triethylamine	101.193	6mL	0.04

Conclusion

The need of this research work was the synthesis and characterization of metal carbon linkages for catalytic applications. Metal carbon complexes were synthesized by using different reaction conditions for novel synthesizes of organometallic compound. Author reported the successful synthesis of novel nitrogen ligand donor which can provide two binding sites for complexation. Thus it is also suggested that such a ligand can show bidentate chelating properties thus as-prepared metal complex have shown enhanced stability. The synthesis of N, N-1,2 (phenylenedipropionamide) was achieved utilizing this approach, which involved the use of carboxylic acid derivatives and toluene as a solvent. The N, N-1,2 (phenylenedipropionamide) synthesized compounds were characterized by using FTIR, XRD, TLC, melting point and catalytic activities. The percentage yield obtained for ligand is 49. In an ethanol solution, SnCl2 and ligand (L) were stirred together to make a metal complex of tin (II). XRD confirmed well-described crystalline peaks indicating that substances have crystalline phase. Metal complex was tested for catalytic activity. Heteroleptic and homoleptic tin (II) bearing guanidinate complexes are used for demonstration of cyclic esters polymerization, resulting in cyclic polymers and copolymers. It is also used for cyclotrimerization of arylisocyanate which are exhibiting excellent catalytic activity.

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