EXPLORATION OF COPPER-BASED COORDINATION POLYMER AS CATALYST: HIGH YIELD OXIDATIVE COUPLING OF BENZYLAMINE TO IMINE

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ABSTRACT

Benzylamine to imine conversion through oxidative coupling reaction has been achieved with almost 91% yield under very mild conditions by applying a one-dimensional coordination polymer as a catalyst and tert-butyl hydroperoxide (TBHP) as an oxidizing agent. The 1D-coordination polymer, \([\text{Cu}_2(2,3\text{-pydc})(2,2^\prime\text{-bpy})(\text{H}_2\text{O})_2]_n(A)\) has been re-synthesized by different synthetic process using the ligands 2,3-pyridinedicarboxylic acid (2,3-pydc) and 2,2^\prime-bipyridine (2,2^\prime-bpy) and it has been characterized by utilizing different physicochemical techniques such as IR-spectroscopy, UV-Vis spectroscopy, elemental analysis and TG-DTA analysis including reestablishment of X-ray single crystal structure. The proposed mechanism of the reaction indicates that the catalytic reaction is facilitated by a flexible and coordinatively unsaturated Cu(II) center and through the formation of tert-butyl peroxy radical.

Keywords: Benzylamine, Imine, 1D-Coordination Polymer, 2,3-Pyridinedicarboxylic Acid, 2,2^\prime-Bipyridine, Cu-Complex, Catalyst.

INTRODUCTION

Synthesis of imine compounds from amines via oxidative coupling reaction is of interest to many researchers nowadays because unsaturated C = N double bonds provide high reactivity and can be used for organic transformation in chemical synthesis.¹,² As a result, imine compounds have been widely used in various fields of applications such as the synthesis of bio-active nitrogen-containing compounds and nitrogen heterocycles,³ medicines, dyes, fragrances, fungicides, agricultural products,⁴ polymers, lipoxygenase inhibitors,⁵ pharmaceuticals,⁶,⁷ anti-inflammatory and anticancer agents.⁸ These nitrogen-based compounds also act as electrophilic reagents in different organic reactions and are also useful intermediates in the racemization of amines.⁹ Conventional method of oxidation of benzylamine to imine is carried out by the use of the stoichiometric amount of metal-oxidants.¹⁰ However, the use of metal oxidants has some disadvantages like high energy consumption, undesirable waste products, difficulty in operating, and purification steps. Among the different methods for synthesizing imine, self-coupling or homo-coupling are generally preferred to other methods as they are used to transform into different products. Different studies reveal that catalytic oxidation of benzylamine to imines is done by using different Cu complexes,¹¹,¹² copper–supported alumina,⁷,¹³-¹⁵ copper, and cerium oxide,¹⁶ and Cu/chitosan beads.¹⁷ Recently 3-dimensional Cu-based metal-organic framework (Cu-MOF) has been employed as a catalyst for the oxidative coupling of benzylamine to an imine.¹²,¹⁸ Various inorganic coordination polymers including MOF have been constructed in the last couple of decades and they are found to be very useful in applications of different fields viz. catalysis,¹⁹-²¹ gas storage and separation,²²,²³ water harvesting,²⁴ antibacterial activity,²⁵,²⁶ magnetism,²⁷ and luminescence²⁵,²⁷ properties as well as in medical field such as drug delivery,²⁸ cancer treatment,²⁹ etc. Various works on different pyridinedicarboxylic acids with different metal complexes have also been reported earlier.³⁰-⁴⁵ but their applications as catalysts for important organic reactions are not explored. The 1D coordination polymer of

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Cu(II) has been synthesized by Yin et al. with 2,3- pyridinedicarboxylic acid (2,3-pydc) and 2,2’-bipyridine (2,2’-bpy) as ligand has only been characterized by single crystal x-ray diffraction study, FTIR spectroscopy, and elemental analysis. The same compound has been re-synthesized using different synthetic technique and further characterizations have been done using UV-Visible spectroscopy, TGA/DTA analysis, X-ray powder diffraction study including reconfirmation of single crystal X-ray data, and FTIR data. Other than the new synthetic methodology, the 1D-coordination polymer has been explored as a catalyst and surprisingly it shows excellent catalytic activity for oxidative coupling of benzylamine to imine. This is the first example, where a Cu-based one-dimensional coordination polymer has been used as a catalyst for such an organic transformation reaction.

EXPERIMENTAL

Materials
All chemicals and solvents are directly purchased and used without any further purification. Cu(ClO₄)₂.6H₂O is purchased from Sigma Aldrich, 2,3-pyridinedicarboxylic (2,3-pydc) acid from Hi media laboratories and 2,2’-bipyridine (2,2’-bpy) from Alfa Aesar. Benzylamine and tert-butyl hydroperoxide 70% in water (TBHP) are purchased from Pallav and Loba Chemie Pvt Ltd respectively. Solvents CH₃OH and DMF are purchased from Emplura. Petroleum Ether and ethyl acetate are purchased from SRL.

Characterization Techniques
FTIR spectroscopy data in the range of 4000 to 400 cm⁻¹ region has been taken using Shimadzu FTIR 8201 spectrophotometer through the KBr pellet. Solid state UV-spectrum has been taken by using Shimadzu UV-2600 UV-Vis spectrophotometer by taking pure BaSO₄ as standard reference material. Elemental analysis has been performed by EuroEA elemental analyzer. Thermal analysis has been performed on SII 6300 EXSTAR thermogravimetric analyzer (heating rate:10°C/min) in a N₂ atmosphere. SC-XRD data is collected on BRUKER D8 VENTURE SC-XRD using dual X-ray sources (Mo-Kα). Molecular drawing is obtained by Mercury 3.8 software. Powder XRD data has been collected on the EMPYREAN Diffractometer system. NMR data has been collected on BRUKER 400MHz (Model: AV400) NMR spectrometer using DMSO-d₆ as solvent.

Synthesis of [{Cu₂(pydc)₂(2,2’-bpy) (H₂O)₂}.4H₂O]ₙ (A)
A mixture of CuClO₄.6H₂O (0.370g, 1 mmol), 2,3-pydc(0.167g, 1mmol), 2,2’-bpy (0.078g, 0.5 mmol) was dissolved in CH₃OH (10ml) and DMF (10ml) with mild heat for 10 to 15 minutes. The solution mixture is then kept undisturbed in an open environment. After several days blue color crystals are obtained in 34.34% yield. The analytical calculation for Cu₂C₂4H₂6N₄O₁₄ (%): C (39.94); N (7.77); H (3.61). Found: C (41.14); N (8.591); H (3).

Study of Catalytic Activity
15 mg of catalyst (compound A) is placed in a round bottom flask containing 10 mmol benzylamine and 15 mmol TBHP. It is observed that as soon as the catalyst is added to the reaction mixture at room temperature (45°C), the reaction starts and the stirring is continued for another half an hour. Thin-Layer Chromatography (TLC) has been used to monitor the reaction. Thereafter the pure product has been isolated using column chromatography with petroleum ether and ethyl acetate solvent system. The formation of imine product is confirmed by NMR spectroscopy using a 400 MHz NMR spectrometer.

RESULTS AND DISCUSSION

FTIR Spectroscopy
The IR spectrum of compound A is taken within the range of 4000 – 400 cm⁻¹ and the peak positions are very much similar to that reported one. The strong and broad peak at around 3344 cm⁻¹ is for water molecules. A very weak peak of νCH appears at the range of 3122 cm⁻¹. The strong and sharp peaks of asymmetric (νas) and symmetric (νs) stretching vibrations of COO⁻ groups appear in the range of 1587 cm⁻¹ and 1394-1336 cm⁻¹ respectively. The presence of two different vibrational peaks of the carboxylate group in the IR spectrum indicates that C – O are in different coordination modes. The comparative reported study of the different free x,y-pyridinedicarboxylic acid, (x, y= 2,3;2,4;3,4) with different
copper (II) pyridinedicarboxylate complexes confirms that the ligand is coordinated to the Cu-metal center.

**UV-Visible Spectroscopy**

The solid-state UV-Visible spectroscopy (200-850nm) is taken at room temperature by taking BaSO$_4$ as a blank reference (Fig.-1). The absorption bands lower than 320 nm are mainly an indication of intra-ligand $\pi - \pi^*$ transitions. In the spectrum of compound A, the $\pi - \pi^*$ transitions are observed at 253 nm and 302 nm respectively. The absorption band at 363 nm is attributed to the ligand-to-metal charge transfer indicating coordination of ligand to the metal center. Very broad band observe in the visible region in the range of 639 – 723 nm is mainly attributed to the d-d transitions.

![Fig.-1: UV-visible Spectrum of Compound A](image_url)

**TGA / DTA Analysis**

The thermal stability of the compound is studied at a temperature range of 30 – 650 °C at the heating rate of 10 °C/ min (Fig.-2). The first step of weight loss occurs at 30 – 110 °C because of the release of six molecules of coordinated and uncoordinated water molecules with a total weight loss of 14.43% (calc. 13.72%). Since the weight loss for six water molecules is taking place in a single step, it may be assumed that at lower temperatures uncoordinated four water molecules are released followed by the release of two coordinated water molecules at higher temperatures and the entire dissociation process is continuous. The dehydrated molecule starts to decompose just above 200 °C and the decomposition process completes at around 415 °C. The dissociation processes for this material are accompanied by endothermic reactions which are confirmed by the DTA curve.

![Fig.-2: TGA/ DTA of Compound A](image_url)

**Single Crystal XRD Analysis**

Compound A has a monoclinic crystal system and the space group is P2$_1$/C, which is similar to the reported one. From the crystallographic analysis, it is seen that the bond lengths and the bond angles are very much similar to that of the reported one. The cell parameters are, $a = 7.7715\ (11)\text{Å}$, $b = 27.468\ (4)\text{Å}$ and $c = 13.285\ (2)\text{Å}$ with $\alpha = \beta = 90^\circ$ but $\gamma = 100.705(4)^\circ$ respectively. Figure-3 shows the coordination of Cu (II) ions with 2, 3-pydc, and 2, 2'-bpy. The 1D zig-zag polymeric chain of the complex along the crystallographic a-axis is also shown in Fig.-4. The Cu…Cu bond distances are found to be 7.941(2) Å and 7.999(1) Å and the volume occupied by the crystal lattice is 2786.6(7)Å$^3$.

**X-ray Powder Diffraction Study**

The X-ray powder diffraction study of bulk compound A has been done to confirm the bulk material is in a single phase and its crystal system is the same as that determined by the X-ray single crystal study. The
stimulated powder (Fig.-5a) pattern derived from X-ray single crystal data (using Mercury 3.8 software) has been compared with the experimental powder pattern (Fig.-5b). It is seen that all the major peaks at 2θ>10° of the experimental XRD pattern of bulk material is matching with the stimulated pattern. This confirms that the synthesized bulk material which has been used as a catalyst are in the same phase and its structure is the same that determined by a single crystal X-ray study.

Fig.-3: ORTEP View of Coordination Polymer of Cu with 20% Ellipsoid Probability. The Lattice Water Molecules and Hydrogen Atoms are not Shown for Clarity

Fig.-4: 1D Zig-Zag Polymeric Chain of \([\{\text{Cu}_3\text{(pydc)}_2(2,2\text{'}-\text{bpy})\text{(H}_2\text{O})_2\}.4\text{H}_2\text{O}\}]_n\) Along Crystallographic a-Axis

Fig.-5a: Stimulated Powder XRD Pattern of Compound A

Fig.-5b: Experimental Powder XRD Pattern of Bulk Compound A
Catalytic Application
Oxidative-Coupling Reactions of Benzylamine to Imine
Many oxidative coupling reactions of benzylamine with different copper-based composite materials as catalysts have been reported.\textsuperscript{13-17} It is also reported that when Cu-BTC MOF is employed for oxidative coupling of benzylamine in acetonitrile at 80°C with O\textsubscript{2} as oxidant gives imine in low yield.\textsuperscript{12} The same reaction in the absence of solvent gives better results.\textsuperscript{12} However, the oxidative coupling reaction of amines at room temperature using Cu-BDC MOF provides high to moderate yield.\textsuperscript{18} Based on the reported experimental results, the synthesized 1D coordination polymer has been explored for oxidative coupling reaction of benzylamine using TBHP as an oxidizing agent in the absence of any solvent. The results of different experiments performed by loading a different number of catalysts are shown in Table-1. Among the different catalysts loading, it is seen that 15mg of catalyst loading shows good catalytic activity with good yield (Table-1, entry-3). To know the effect of the catalyst, the blank experiment is also performed which shows no effect \textit{i.e.} no product is formed (Table-1, entry-5) at the same reaction condition.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst (mg)</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>Benzylamine</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Benzylamine</td>
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</tr>
<tr>
<td>5</td>
<td>Benzylamine</td>
<td>-</td>
<td>0</td>
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Table-1: Optimization of Reaction Parameters of Oxidation of Benzylamine

Reaction conditions: Benzylamine (10 mmol), TBHP (15mmol), Temperature (45°C) in the absence of solvent

Confirmation of Imine Product
The formation of imine product (N-benzylbenzaldimine) has been established by \textsuperscript{1}H NMR as well as \textsuperscript{13}C NMR spectra. The chemical shift position values(δ) of both \textsuperscript{1}H NMR and \textsuperscript{13}C NMR with respect to Tetramethylsilane (TMS) in DMSO solvent are given below:

\textsuperscript{1}H NMR (400 MHz, DMSO): δ 8.491 (s, 1H), 7.804-7.445 (m, 5H), 7.345-7.230 (m, 5H), 4.77 (s, 2H).


Mechanism of the Catalytic Reaction
The probable mechanism for the oxidation of benzylamine to N-benzylbenzaldimine with TBHP as an oxidant in the presence of a catalyst (A) is shown in Scheme-1.
A similar type of mechanism has also been adopted by Anbardan et al. The five coordinated Cu centres of the catalyst are believed to be the active site of the catalytic reaction since both the Cu centres are coordinatively unsaturated, which create enough opportunity for the substrate to get coordinated with Cu. From the crystal structure (Fig.-3) it is confirmed that there are two types of Cu(II) centers available in the molecule and it is believed that Cu1 is less active as a catalytic site due to the less flexibility surrounding its coordination zone (because of the presence of two stable pentagonal rings) whereas Cu2 is assumed to be more catalytically active due to higher flexibility surrounding it’s coordination zone (because of the presence of one pentagonal ring formed by 2,2'-bpy). The mechanism shows that the catalyst A, oxidized TBHP into tert-butylperoxy radical. This radical then abstract hydrogen from benzylamine, and convert to 1b which subsequently transform into imine 1c by elimination of TBHP. Further addition of benzylamine to imine along with removal of ammonia results N-benzylbenzaldimine 2.

CONCLUSION

We have successfully redeveloped Cu(II) coordination polymer with 2,3-pydc and 2,2'-bpy by following a new synthetic route. Other than single crystal X-ray analysis, FTIR study and elemental analysis, the compound (A) has been further characterized by TGA/DTA analysis, UV-Visible spectroscopy and X-ray powder diffraction study. The purity of bulk material has been confirmed by comparing the experimental powder X-ray data with stimulated one from single crystal X-ray data. After full characterization, this one-dimensional Cu-based coordination polymer has been explored as catalyst for oxidative coupling of benzylamine to imine product with probable reaction mechanism. The catalytic study shows good yield of 91% imine product even at room temperature in absence of solvent.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in experimental work, data analysis and interpretation, reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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