Electronic Supplementary Information

A binuclear Mn(II) complex as an efficient catalyst for transamidation of carboxamides with amines

Divya Pratap Singh, Bharat Kumar Allam, Krishna Nand Singh and Vinod Prasad Singh*

Department of Chemistry (Centre of Advanced Study), Faculty of Science, Banaras Hindu University, Varanasi 221005, India

*E mail: singvp@yahoo.co.in
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1. General information

Infrared spectra were recorded in KBr on a Varian 3100 FT-IR spectrophotometer in 4000-400 cm\(^{-1}\) region. An electronic spectrum of the complex was recorded on a Shimadzu spectrophotometer model Pharmaspec UV-1700 in nujol. The C, H and N contents were determined on an Exeter Analytical Inc. CHN Analyzer (Model CE-440). Magnetic susceptibility measurement was performed at room temperature on a Faraday balance using Hg[Co(SCN)]\(_4\) as the calibrant and corrected for diamagnetism.\(^1\) All the transamidation experiments were carried out under open atmosphere by using standard Schlenk technique. Column chromatography was carried out employing Merck silica gel (100-120 mesh). Pre-coated Merck GF\(_{254}\) plates (thickness 0.25 mm) were used for thin-layer analytical chromatography. Visualization of spots on TLC plate was accomplished with UV light and by staining in iodine chamber.\(^1\)\(^\text{H}\) and \(^{13}\)C NMR were recorded on JEOL AL300 FT-NMR spectrometer. \(^1\)H frequency is at 300.40 MHz and \(^{13}\)C frequency is at 75.45 MHz. \(^1\)H and \(^{13}\)C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak as follows: DMSO-\(d_6\) = 2.50 (\(^1\)H NMR); DMSO-\(d_6\) = 39.50 (\(^{13}\)C NMR). Product yields refer to isolated yields after column chromatography.

Single crystal X-ray diffraction data of ligand \(\text{H}_2\text{bpoh}\) and the complex \([\text{Mn}(\text{Hbpoh})(\text{OAc})(\text{H}_2\text{O}))\text{\_2\_6H}\text{_2O}\) were obtained at 295(2) K, on a Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite mono-chromated Mo-K\(\alpha\) (\(\lambda = 0.71073\ \text{Å}\)) radiation source. The structures were solved by direct methods (SHELXL-97) and refined against all data by full matrix least-square on \(F^2\) using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model.\(^2,3\) The MERCURY package and ORTEP-3 for Windows program were used for generating structures.\(^4,5\)

2. Reagents

All the chemicals are of analytical grade and were purchased from various commercial sources and used without further purification. 2-bezoylpyridine and oxalic acid dihydrazide were obtained from Sigma-Aldrich, USA; MnCl\(_2\cdot4\text{H}_2\text{O}\), Mn(OAc)\(_2\cdot4\text{H}_2\text{O}\), MnO\(_2\), Mn(NO\(_3\))\(_2\cdot4\text{H}_2\text{O}\) and solvents were obtained from Merck Chemicals, India.

3. Synthesis and characterization of ligand \(\text{H}_2\text{bpoh}\)

(a) Procedure for synthesis of \(\text{H}_2\text{bpoh}\)

The ligand, \((\text{N'}1\text{E, N'}2\text{E})\cdot\text{N'}1,\text{N'}2\cdot\text{bis(phenyl (pyridin-2-yl)methylen})\cdot\text{oxalohydrazide (H}_2\text{bpoh})\) was prepared by reacting 50 mL aqueous solution of oxalic acid dihydrazide (5 mmol, 0.59 g) with 25 mL methanolic solution of 2-bezoylpyridine (10 mmol, 1.83 g) in 1:2 molar ratio in a round bottom flask. The reaction mixture was
refluxed continuously for 20 h. A white solid product was obtained on cooling the above solution at room temperature. The product was filtered on a Buckner funnel through suction and purified by washing several times with water followed by methanol to remove the unreacted components. The pure compound was dried in a desiccator over anhydrous CaCl$_2$ at room temperature. Single crystal of the ligand H$_2$bpoh was obtained from a mixture of dichloromethane and DMSO solution by slow evaporation at room temperature.

**(b) Characterization data of H$_2$bpoh** Yield (80%), m. p. 292 °C. Anal. Calc. for C$_{26}$H$_{20}$N$_6$O$_2$ (448.48): C, 69.63; H, 4.49; N, 18.74. Found: C, 69.55; H, 4.47; N, 18.71%. IR (ν cm$^{-1}$, KBr): ν(NH) 3387(b); ν(C=O) 1690(s); ν(C=N) 1582(m); ν(N−N) 994(w). $^1$H NMR (DMSO-$d_6$; δ ppm): 14.08$^#$ (br s, 2H, NH, Z), 10.28 (br s, 2H, NH, E); 8.89–7.39 (m, 18H, Ar-H). $^{13}$C NMR (DMSO-$d_6$; δ ppm): 160.79, 157.48, 150.70, 148.40, 148.25, 137.33, 136.30, 135.90, 128.90, 128.28, 127.83, 127.66, 125.16, 124.37.

$^#$The appearance of NH proton signal at higher ppm (14.08) is due to involvement in intra-molecular H-bonding with pyridine-N in Z form.

4. **Crystal structure of ligand H$_2$bpoh**

The ORTEP diagram of ligand with the atomic numbering scheme is shown (Fig. 1). The molecule displays a E configuration about the >C=N bond. The >C=O and >C=N displays a bond distance of 1.208(5) Å and 1.294(5) Å, respectively which is consistent with a double bond. The N(2)-N(3) bond distance is 1.372(5) Å, which is slightly shorter than the single bond, showing some double bond character. Due to the presence of intra-molecular N(3)-H···N(1) hydrogen bond, Py−C(6)=N(2)−N(3)=C(13)=O(1) skeleton in the ligand is almost planar. The intra-molecular hydrogen bond N(3)−H(3A)···N(1), is formed between N(3)−H(3A) of amido-N atom and the nitrogen of pyridine ring. The torsion angles N(1)−C(5)−C(6)−C(7) [174.6(5)$^\circ$], O(1)−C(13)−N(3)−N(2) [1.8(8)$^\circ$], N(1)−C(5)−C(6)−N(2) [−5.7(8)$^\circ$] and N(3)−N(2)−C(6)−C(7) [179.9(4)$^\circ$] indicate that O(1)−N(2) and N(1)-N(2) are syn-periplanar to each other but N(1)−C(7) and N(3)−C(7) are anti-periplanar to each other.
5. Synthesis and characterization of Mn(II) complex

(a) Procedure for synthesis of Mn(II) complex The [Mn(Hbpo)(OAc)(H\textsubscript{2}O)]\textsubscript{2} \cdot 6H\textsubscript{2}O was synthesized by reacting 50 mL methanolic solution of Mn(II) acetate (5 mmol, 1.23 g) with 50 mL hot methanolic solution of the ligand H\textsubscript{2}bpo (5 mmol, 2.24 g) in 1:1 (M:L) molar ratio in a round bottom flask. The reaction mixture was refluxed for 2 h and then cooled at room temperature. The pure complex was crystallized by slow evaporation of the solvent at room temperature.

(b) Characterization of Mn(II) complex Yield (65%), Pink, m. p. 185 °C. \(\mu\text{eff} = 5.95\) B.M. Anal. Calc. for C\textsubscript{56}H\textsubscript{60}Mn\textsubscript{2}N\textsubscript{12}O\textsubscript{16} (1267.04): Mn, 8.67; C, 53.09; H, 4.77; N, 13.27. Found: Mn, 8.70; C, 53.12; H, 4.74; N, 13.24%. IR (\textnu cm\textsuperscript{-1}, KBr): \textnu(OH) 3433 (b); \textnu(NH) 3301 (w); \textnu(C=O) 1686 (s); \textnu(C=N) 1580 (s); \textnu(C=N) 1567 (m); \textnu(C=N-CO\textsuperscript{−}) 1547 (m); \textnu(C-O\textsuperscript{−}) 1250(w); \textnu(N-N) 1024 (w).
6. Packing diagram of Mn(II) complex

Fig. S3 Packing diagram of Mn(II) complex

7. Inter- and intra-molecular H-bonding in Mn(II) complex

Fig. S4 Inter- and intra-molecular hydrogen bonding leading to five member water clusters
### 8. Selected crystallographic data for ligand and Mn(II) complex

**Table 1** Crystallographic data of the ligand and complex

<table>
<thead>
<tr>
<th></th>
<th>H₂bpoh</th>
<th>[Mn(Hbpoh)(OAc)(H₂O)]₂·6H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C₂₆H₂₀N₆O₂</td>
<td>C₅₆H₆₀Mn₂N₁₂O₁₆</td>
</tr>
<tr>
<td>Formula weight</td>
<td>448.48</td>
<td>1267.04</td>
</tr>
<tr>
<td>Temp, K</td>
<td>293</td>
<td>293</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P - 1</td>
<td>P - 1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.000(10)</td>
<td>11.6403(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>15.6555(16)</td>
<td>12.6172(10)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>16.5447(16)</td>
<td>12.7323(9)</td>
</tr>
<tr>
<td>α (°)</td>
<td>115.226(10)</td>
<td>60.362(2)</td>
</tr>
<tr>
<td>β (°)</td>
<td>101.302(8)</td>
<td>73.137(2)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>98.774(9)</td>
<td>63.765(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2214.9(5)</td>
<td>1451.75(19)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>D&lt;sub&gt;calc&lt;/sub&gt; (g/cm³)</td>
<td>1.345</td>
<td>1.431</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>0.089</td>
<td>0.514</td>
</tr>
<tr>
<td>F(000)</td>
<td>936</td>
<td>642</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.24x 0.22x</td>
<td>0.34x 0.32x 0.30</td>
</tr>
<tr>
<td>θ range for data collection (°)</td>
<td>2.93 - 29.15</td>
<td>3.24 - 27.44</td>
</tr>
<tr>
<td>No. of reflections collected</td>
<td>19908</td>
<td>14320</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>11941</td>
<td>6561 (0.0568)</td>
</tr>
</tbody>
</table>
(R_int) (0.0821)
Number of data/restraints/parameters 11941 / 6 / 614 6561/7/393
Goodness-of-fit on F^2 0.910 1.085
R1, wR2^a,b [(I>2σ(I))] 0.0766, 0.0809 0.0776, 0.2243
R1, wR2^a,b (all data) 0.3186, 0.1391 0.1092, 0.2590
Largest difference in peak and hole (e.Å^-3) 0.178 and -1.620 and -0.736 0.177

^a R1 = Σ||Fo| − |Fc||Σ|Fo|; ^b R2 = [ΣW(|F_o|^2 − |F_c|^2)^2 / ΣW|F_o|^2]^{1/2}

Table 2 Selected bond lengths and bond angles

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>H2bpoh</th>
<th>[Mn(Hbpoh)(OAc)(H2O)]_2·6H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)–C(13)</td>
<td>1.208(5)</td>
<td>1.260(4)</td>
</tr>
<tr>
<td>N(3)–C(13)</td>
<td>1.352(5)</td>
<td>1.310(5)</td>
</tr>
<tr>
<td>N(3)–N(2)</td>
<td>1.372(5)</td>
<td>1.393(5)</td>
</tr>
<tr>
<td>N(2)–C(6)</td>
<td>1.294(5)</td>
<td>1.286(5)</td>
</tr>
<tr>
<td>C(5)–C(6)</td>
<td>1.497(6)</td>
<td>1.480(6)</td>
</tr>
<tr>
<td>C(5)–N(1)</td>
<td>1.347(6)</td>
<td>1.351(4)</td>
</tr>
<tr>
<td>N(1)–C(1)</td>
<td>1.325(6)</td>
<td>1.340(6)</td>
</tr>
<tr>
<td>C(6)–C(7)</td>
<td>1.474(7)</td>
<td>1.496(4)</td>
</tr>
<tr>
<td>Mn(1)–O(1)</td>
<td>2.209(4)</td>
<td></td>
</tr>
<tr>
<td>Mn(1)–O(1)^i</td>
<td>2.188(3)</td>
<td></td>
</tr>
</tbody>
</table>
\begin{itemize}
  \item Mn(1)–O(3)  \hspace{1cm} 2.178(5)
  \item Mn(1)–O(5)  \hspace{1cm} 2.225(6)
  \item Mn(1)–N(1)  \hspace{1cm} 2.307(4)
  \item Mn(1)–N(2)  \hspace{1cm} 2.323(2)

\textbf{Bond Angle}

\begin{align*}
  \text{O(1)–C(13)–N(3)} & \quad 127.1(5) \quad 126.5(4) \\
  \text{N(3)–N(2)–C(6)} & \quad 120.1(4) \quad 119.3(3) \\
  \text{C(5)–N(1)–C(1)} & \quad 118.2(5) \quad 118.2(4) \\
  \text{C(13)–N(3)–N(2)} & \quad 118.3(4) \quad 107.5(3) \\
  \text{O(1)–Mn(1)–O(3)} & \quad 95.1(1) \\
  \text{O(1)–Mn(1)–O(5)} & \quad 86.7(1) \\
  \text{O(1)–Mn(1)–N(2)} & \quad 133.2(1) \\
  \text{O(1)–Mn(1)–N(1)} & \quad 156.8(1) \\
  \text{O(1)–Mn(1)–O(1)} & \quad 66.6(1) \\
  \text{O(3)–Mn(1)–O(5)} & \quad 162.7(2) \\
  \text{O(3)–Mn(1)–N(2)} & \quad 99.5(1) \\
  \text{O(3)–Mn(1)–N(1)} & \quad 84.8(2) \\
  \text{O(3)–Mn(1)–O(1)} & \quad 102.2(1) \\
  \text{O(5)–Mn(1)–N(2)} & \quad 91.7(1) \\
  \text{O(5)–Mn(1)–N(1)} & \quad 86.9(2) \\
  \text{O(5)–Mn(1)–O(1)} & \quad 94.3(1) \\
  \text{N(2)–Mn(1)–N(1)} & \quad 69.2(1) \\
  \text{N(2)–Mn(1)–O(1)} & \quad 66.9(1) \\
  \text{N(1)–Mn(1)–O(1)} & \quad 136.1(1) \\
  \text{Mn(1)–O(1)–Mn(1)} & \quad 113.4(1)
\end{align*}
\end{itemize}
9. Catalytic activity test

(a) Procedure for transamidation [Mn(Hbpoh)(OAc)(H₂O)]₂·6H₂O (5 mol%) was added to a Schlenk flask, equipped with a rubber septum and teflon-coated stir bar, containing carboxamide (10 mmol) and amine (10 mmol). The resulting mixture was vigorously stirred at 120 °C for 24 h. The progress of the reaction was monitored through TLC. After completion of the reaction, the resulting mixture was cooled to room temperature; ethyl acetate (20 mL) was added and filtered through a porous plug. The filtrate was concentrated using rotary vacuum evaporator. The crude product thus obtained was purified by column chromatography using a mixture of ethyl acetate/n-hexane as an eluent. All the products have been full characterized on the basis of their physical and spectral properties.

10. References


