

Electronic Supplementary Information

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

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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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ 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 GF₂₅₄ 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. ¹H and ¹³C NMR were recorded on JEOL AL300 FT-NMR spectrometer. ¹H frequency is at 300.40 MHz and ¹³C frequency is at 75.45 MHz. ¹H and ¹³C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak as follows: DMSO-*d*₆ = 2.50 (¹H NMR); DMSO-*d*₆ = 39.50 (¹³C NMR). Product yields refer to isolated yields after column chromatography.

Single crystal X-ray diffraction data of ligand H₂bpoh and the complex $[\text{Mn}(\text{Hbpoh})(\text{OAc})(\text{H}_2\text{O})]_2 \cdot 6\text{H}_2\text{O}$ were obtained at 295(2) K, on a Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite mono-chromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) 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; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, MnO_2 , $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and solvents were obtained from Merck Chemicals, India.

3. Synthesis and characterization of ligand H₂bpoh

(a) Procedure for synthesis of H₂bpoh

The ligand, (N'1E,N'2E)-N'1,N'2-bis(phenyl (pyridin-2-yl)methylene)oxalohydrazide (H₂bpoh) 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_2bpoh was obtained from a mixture of dichloromethane and DMSO solution by slow evaporation at room temperature.

(b) Characterization data of H_2bpoh Yield (80%), m. p. 292 °C. *Anal.* Calc. for $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_2$ (448.48): C, 69.63; H, 4.49; N, 18.74. Found: C, 69.55; H, 4.47; N, 18.71%. IR ($\nu \text{ cm}^{-1}$, KBr): $\nu(\text{NH})$ 3387(b); $\nu(\text{C=O})$ 1690(s); $\nu(\text{C=N})$ 1582(m); $\nu(\text{N-N})$ 994(w). ^1H NMR ($\text{DMSO-}d_6$; 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 ($\text{DMSO-}d_6$; 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.⁶

4. Crystal structure of ligand H_2bpoh

The ORTEP diagram of ligand with the atomic numbering scheme is shown (Fig. 1). The molecule displays a E configuration about the $>\text{C}=\text{N}$ bond.⁷ The $>\text{C}=\text{O}$ and $>\text{C}=\text{N}$ displays a bond distance of 1.208(5) Å and 1.294(5) Å, respectively which is consistent with a double bond.⁸ 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)°], O(1)-C(13)-N(3)-N(2) [1.8(8)°], N(1)-C(5)-C(6)-N(2) [-5.7(8)°] and N(3)-N(2)-C(6)-C(7) [179.9(4)°] 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.

6. Packing diagram of Mn(II) complex

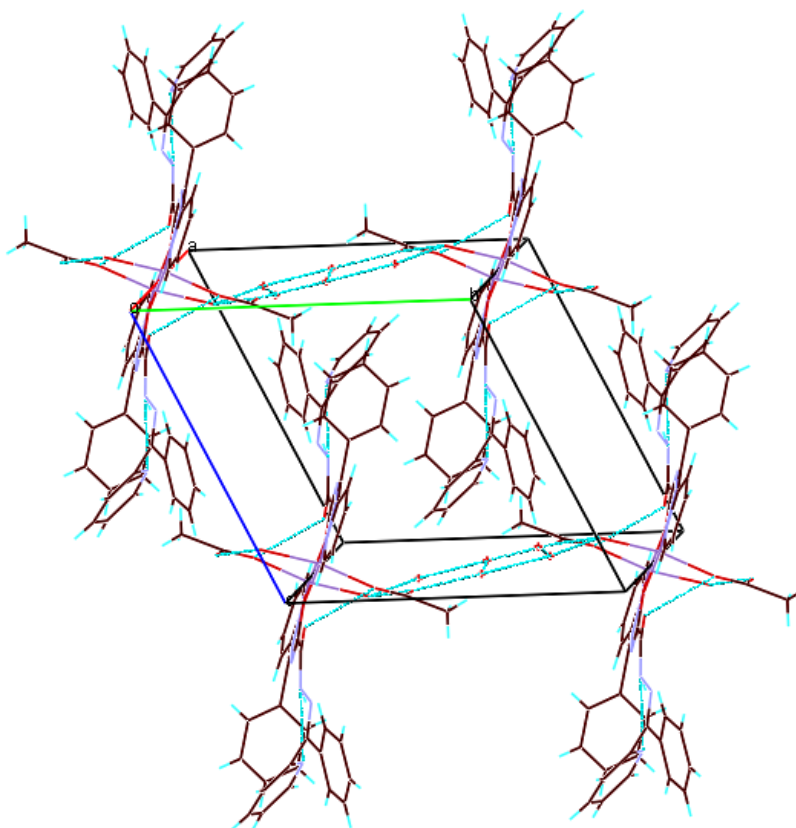


Fig. S3 Packing diagram of Mn(II) complex

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

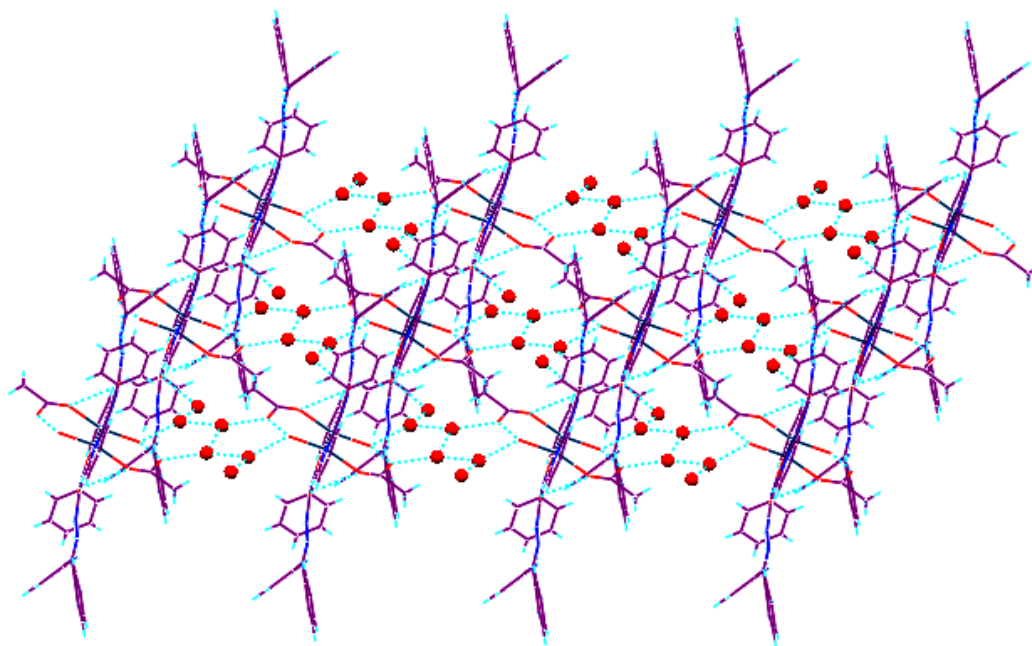


Fig. S4 Inter- and intra-molecular hydrogen bonding leading to five member water clusters

8. Selected crystallographic data for ligand and Mn(II) complex

Table 1 Crystallographic data of the ligand and complex

	H₂bpoH	[Mn(HbpoH)(OAc)(H₂O)]₂·6H₂O
Empirical Formula	C ₂₆ H ₂₀ N ₆ O ₂	C ₅₆ H ₆₀ Mn ₂ N ₁₂ O ₁₆
Formula weight	448.48	1267.04
Temp, K	293	293
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P -1
a (Å)	10.000(10)	11.6403(9)
b (Å)	15.6555(16)	12.6172(10)
c (Å)	16.5447(16)	12.7323(9)
α (°)	115.226(10)	60.362(2)
β (°)	101.302(8)	73.137(2)
γ (°)	98.774(9)	63.765(2)
V (Å ³)	2214.9(5)	1451.75(19)
Z	4	1
D _{calc} (g/cm ³)	1.345	1.431
μ (mm ⁻¹)	0.089	0.514
F(000)	936	642
Crystal size (mm)	0.24x 0.22x 0.20	0.34x 0.32x 0.30
θ range for data collection (°)	2.93 - 29.15	3.24 - 27.44
No. of reflections collected	19908	14320
No. of independent reflections	11941	6561 (0.0568)

(R _{int})	(0.0821)	
Number of	11941 / 6 /	
data/restraints/parameters	614	6561/7/393
Goodness-of-fit on F ²	0.910	1.085
R ₁ , wR ₂ ^{a,b} [(I>2σ(I))]	0.0766, 0.0809	0.0776, 0.2243
R ₁ , wR ₂ ^{a,b} (all data)	0.3186, 0.1391	0.1092, 0.2590
Largest difference in peak and hole (e.Å ⁻³)	0.178 and - 0.177	1.620 and -0.736

^a $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; ^b $R_2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)|^2]}{\sum w|F_o|^2}]^{1/2}$

Table 2 Selected bond lengths and bond angles

	H ₂ bpoH	[Mn(HbpoH)(OAc)(H ₂ O)] ₂ ·6H ₂ O
Bond Length		
O(1)–C(13)	1.208(5)	1.260(4)
N(3)–C(13)	1.352(5)	1.310(5)
N(3)–N(2)	1.372(5)	1.393(5)
N(2)–C(6)	1.294(5)	1.286(5)
C(5)–C(6)	1.497(6)	1.480(6)
C(5)–N(1)	1.347(6)	1.351(4)
N(1)–C(1)	1.325(6)	1.340(6)
C(6)–C(7)	1.474(7)	1.496(4)
Mn(1)–O(1)		2.209(4)
Mn(1)–O(1) ⁱ		2.188(3)

Mn(1)–O(3)		2.178(5)
Mn(1)–O(5)		2.225(6)
Mn(1)–N(1)		2.307(4)
Mn(1)–N(2)		2.323(2)
Bond Angle		
O(1)–C(13)–N(3)	127.1(5)	126.5(4)
N(3)–N(2)–C(6)	120.1(4)	119.3(3)
C(5)–N(1)–C(1)	118.2(5)	118.2(4)
C(13)–N(3)–N(2)	118.3(4)	107.5(3)
O(1)–Mn(1)–O(3)		95.1(1)
O(1)–Mn(1)–O(5)		86.7(1)
O(1)–Mn(1)–N(2)		133.2(1)
O(1)–Mn(1)–N(1)		156.8(1)
O(1)–Mn(1)–O(1)		66.6(1)
O(3)–Mn(1)–O(5)		162.7(2)
O(3)–Mn(1)–N(2)		99.5(1)
O(3)–Mn(1)–N(1)		84.8(2)
O(3)–Mn(1)–O(1)		102.2(1)
O(5)–Mn(1)–N(2)		91.7(1)
O(5)–Mn(1)–N(1)		86.9(2)
O(5)–Mn(1)–O(1)		94.3(1)
N(2)–Mn(1)–N(1)		69.2(1)
N(2)–Mn(1)–O(1)		66.9(1)
N(1)–Mn(1)–O(1)		136.1(1)
Mn(1)–O(1)–Mn(1)		113.4(1)

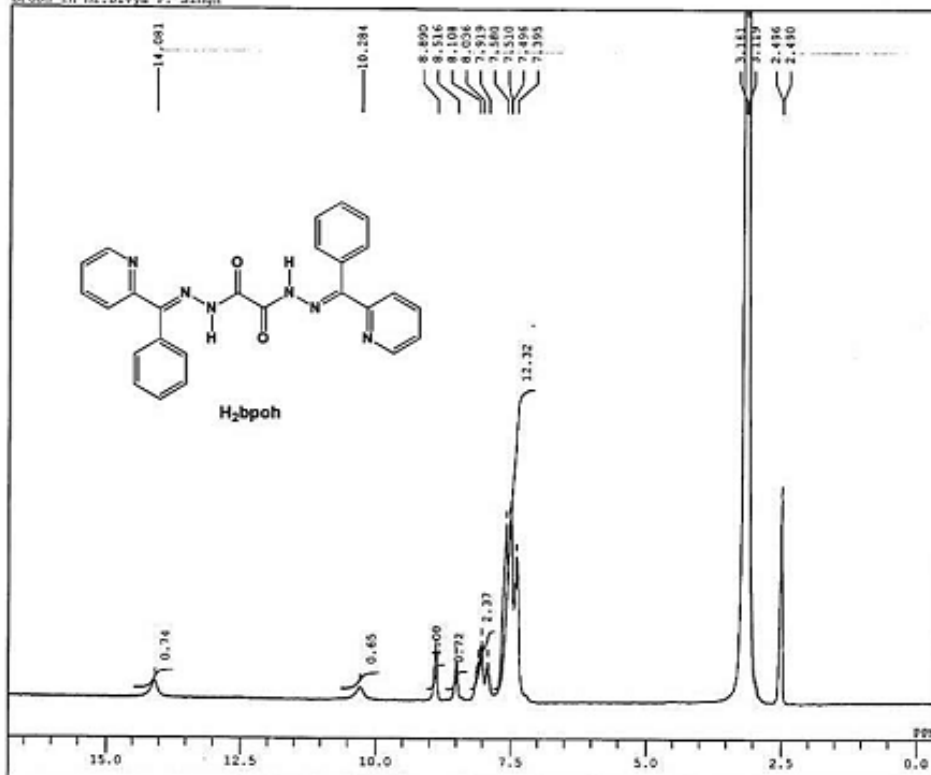
9. Catalytic activity test

(a) Procedure for transamidation $[\text{Mn}(\text{Hbpoh})(\text{OAc})(\text{H}_2\text{O})]_2 \cdot 6\text{H}_2\text{O}$ (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

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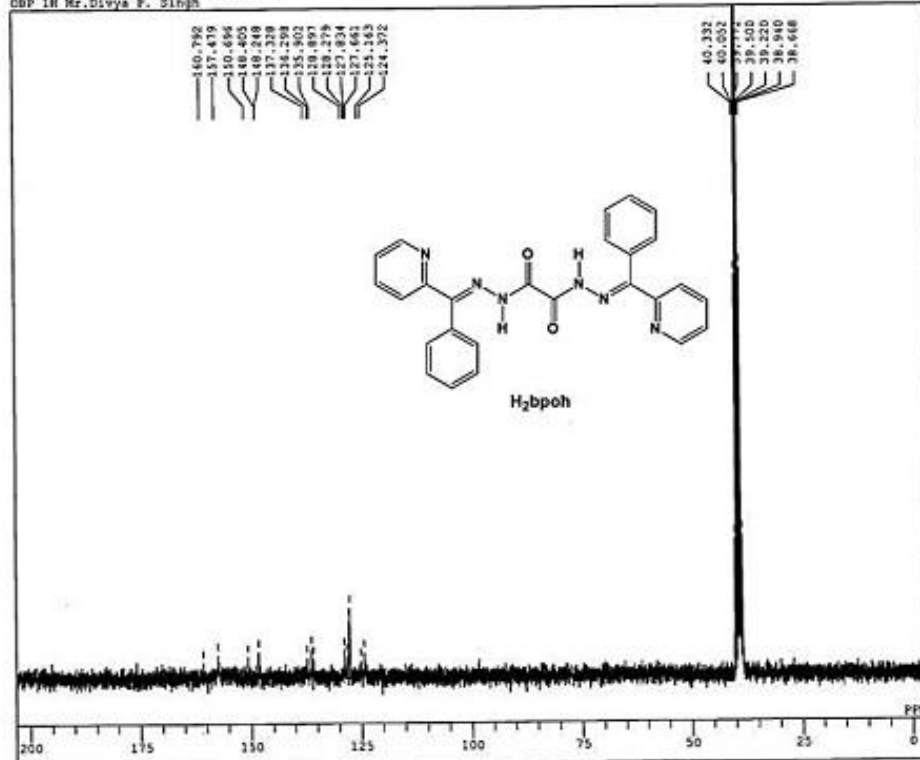


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 CHEMISTRY DEPARTMENT
 Banaras Hindu University,
 VARANASI-221005

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 Shishir Singh

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JEOL AL300 FTMR
 CHEMISTRY DEPARTMENT
 Banaras Hindu University,
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Operator : Nagendra Kumar
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