

Synthesis and catalytic activity of metallo-organic complexes bearing 5-amino 2-ethylpyridine -2-carboximidate

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Abstract. A series of copper, cobalt, nickel and manganese complexes were synthesized and characterized. Reaction of 5-amino-2-cyanopyridine with $MCl_2 \cdot xH_2O$ (M : Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+}) in anhydrous ethanol resulted in the formation of four complexes $[NH_2EtPyCuCl_2(CH_3OH)] \cdot H_2O$ **1**, $[(NH_2EtPyHCl)_3Co](Cl)_3 \cdot 3H_2O$ **2**, $[(NH_2EtPy)_2 2(H_2O)Ni](Cl)_2$ **3**, and $[(NH_2EtPy)_2 2(H_2O)Mn](Cl)_2$ **4** [$NH_2EtPy=5$ -amino-*o*-ethylpyridine-2-carboximidate], respectively. The structures of these compounds were determined by X-ray diffraction, NMR and IR spectroscopy, and elemental analysis. Each complex was then used as a catalyst in the Henry reaction, and its catalytic activity was determined by 1H NMR. Good catalytic effects were achieved (69–87%).

Keywords. 5-amino-2-cyanopyridine; metal complex; NH_2EtPy ; the Henry reaction.

1. Introduction

Copper, cobalt, nickel and manganese complexes involving carboximidate have drawn much attention in the fields of organic synthesis and pharmaceuticals.^{1–7} This is due to the importance of the carboximide ester structural unit as an intermediate or ligand in these fields. For example, this unit can be used as the catalyst for the atom transfer radical polymerization of methyl methacrylate,⁸ or as a new class of chiral Lewis acid catalysts for highly enantioselective hetero-Diels-Alder reactions.⁹ The crystal structure of a similar complex involving *O*-methylpyridine-2-carboximidate was reported in 1995 by M. Jamnicky.¹⁰ Inspired by that pioneering work, herein, we describe for the first time the synthesis and characterization of some copper(II), cobalt(II), nickel(II) and manganese(II) complexes that contain 5-amino-2-cyanopyridine. The complexes were formed in systems containing 5-amino-2-cyanopyridine, metal(II) salts, and anhydrous ethanol and without any catalyst. Additionally, we also used these complexes to catalyze the Henry reaction and achieved good catalytic effects.

2. Experimental

5-amino-2-cyanopyridine, $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ were purchased from

Acros, Aldrich, Fluka, and Sinopharm Chemical Reagent Company, 1H NMR spectra were obtained using a Bruker AM-300 spectrometer. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer and peaks are reported in cm^{-1} . Elemental analysis was performed on VARIO ELIII elemental analyzer. Crystal structure was determined by Gemini S Ultra diffractometer.

2.1 Structure determination

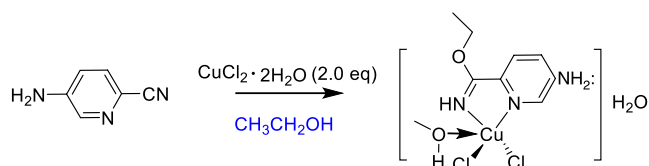
The green crystal of compound **1** with approximate dimensions of $0.230 \times 0.180 \times 0.110$ mm was selected for the data collection on a ‘graphite’ diffractometer with mirror monochromated (MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$). A total of 8273 reflections were collected in a range of $2.094 < \theta < 26.000^\circ$ by using “ ω and Φ ” scan techniques at 293(2) K, $M = 349.69$, Monoclinic, $P 2_1/n$, $a = 7.1949(9) \text{ \AA}$, $\alpha = 90^\circ$, $b = 12.3806(3) \text{ \AA}$, $\beta = 93.630(3)^\circ$, $c = 15.758(2) \text{ \AA}$, $\gamma = 90^\circ$, $V = 1400.9(3) \text{ \AA}^3$, $Z = 4$, $D_{calc.} = 1.658 \text{ Mg/m}^3$, and the final R factor was $R_1 = 0.0290$, 2754 reflections were observed with $I_0 > 2\sigma(I_0)$, $R_\omega = 0.0769$ for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGRAM.⁹

The purple red crystal of compound **2** with approximate dimensions of $0.180 \times 0.150 \times 0.150$ mm was selected for the data collection. A total of 26140

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reflections were collected in a range of $4.270 < \theta < 65.479^\circ$ by using “ ω and Φ ” scan techniques at 296(2) K, $M = 735.96$, Monoclinic, $P 2_1/n$, $a = 13.5023(12) \text{ \AA}$, $\alpha = 90^\circ$, $b = 16.0669(15) \text{ \AA}$, $\beta = 90^\circ$, $c = 16.1341(14) \text{ \AA}$, $\gamma = 90^\circ$, $V = 3500.1(5) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc.}} = 1.397 \text{ Mg/m}^3$, and the final R factor was $R_1 = 0.0706$, 5372 reflections were observed with $I_0 > 2\sigma(I_0)$, $R_w = 0.1665$ for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGRAM.¹¹

The light green crystal of compound **3** with approximate dimensions of $0.30 \times 0.280 \times 0.250 \text{ mm}$ was selected for the data collection. A total of 13927 reflections were collected in a range of $1.841 < \theta < 30.898^\circ$ by using “ ω and Φ ” scan techniques at 296.15 K, $M = 496.04$, Monoclinic, $C 1 2/c 1$, $a = 17.460(4) \text{ \AA}$, $\alpha = 90^\circ$, $b = 15.106(3) \text{ \AA}$, $\beta = 111.516(4)^\circ$, $c = 11.039(2) \text{ \AA}$, $\gamma = 90^\circ$, $V = 2708.7(10) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc.}} = 1.216 \text{ Mg/m}^3$ and the final R factor was $R_1 = 0.0475$, 4242 reflections were observed with $I_0 > 2\sigma(I_0)$, $R_w = 0.1122$ for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGRAM.¹¹



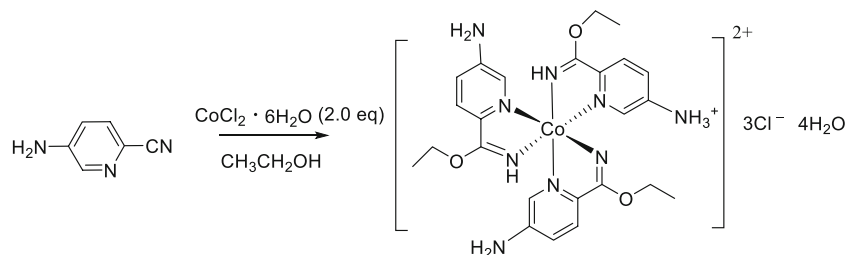
Scheme 1. The synthetic route for complex **1**. Reagents and conditions: ethanol, 80–90°C, 48 h.

The yellow crystal of compound **4** with approximate dimensions of $0.170 \times 0.150 \times 0.110 \text{ mm}$ was selected for the data collection. A total of 7967 reflections were collected in a range of $2.330 < \theta < 25.492^\circ$ by using “ ω and Φ ” scan techniques at 293(2) K, $M = 545.31$, Monoclinic, $C 2/c$, $a = 18.115(17) \text{ \AA}$, $\alpha = 90^\circ$, $b = 15.077(14) \text{ \AA}$, $\beta = 111.733(19)^\circ$, $c = 11.084(10) \text{ \AA}$, $\gamma = 90^\circ$, $V = 812(5) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc.}} = 1.288 \text{ Mg/m}^3$, and the final R factor was $R_1 = 0.065$, 4242 reflections were observed with $I_0 > 2\sigma(I_0)$, $R_w = 0.1674$ for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGRAM.¹¹

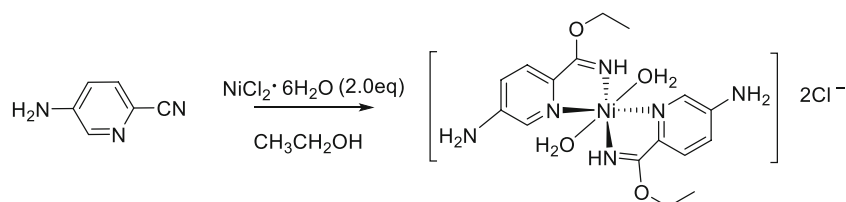
2.2 Preparation of complexes

2.2a Complex 1: 0.5010 g (4.20 mmol) 5-amino-2-cyanopyridines and 40 mL anhydrous ethanol were dispersed in a 100 mL round bottom flask. Then, 1.4346 g (8.40 mmol) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added into the above solution. The mixture was refluxed for 48 h (80–90°C). After hot filtration, residue was obtained. Recrystallization with anhydrous methanol afforded blue crystals. Yield: 42%. M.p.: 158–162°C Elemental analysis: Anal. Calc. for $\text{C}_9\text{H}_{17}\text{Cl}_2\text{CuN}_3\text{O}_3$: C, 30.09; H, 4.86; N, 12.00%; Found: C, 31.39; H, 4.39; N, 12.42%. IR (KBr, pellet, ν/cm^{-1}): 3425, 3324, 3218, 1634, 1590, 1470, 1423, 1390, 1311, 1289, 1147, 1014, 883, 853, 677, 528, 491.

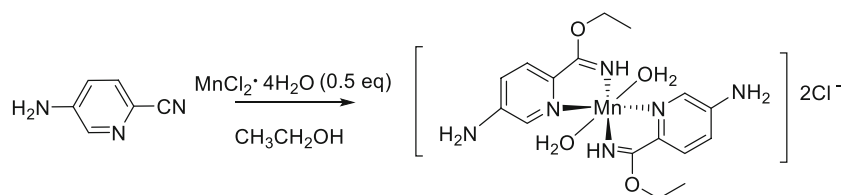
2.2b Complex 2: 0.5962 g (5.0 mmol) 5-amino-2-cyanopyridines and 40 mL anhydrous ethanol were



Scheme 2. The synthetic route for complex **2**. Reagents and conditions: ethanol, 80–90°C, 48 h.



Scheme 3. The synthetic route for complex **3**. Reagents and conditions: ethanol, 80–90°C, 48 h.



Scheme 4. The synthetic route for complex **4**. Reagents and conditions: ethanol, 80–90°C, 48 h.

dispersed in a 100 mL round bottom flask, then 2.3798 g (10.0 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added into the above solution. The mixture was refluxed for 48 h (80–90°C). After hot filtration, the solution was evaporated slowly in the air, to afford the solid. Recrystallization with anhydrous methanol yielded purple red crystals. Yield: 32%. M.p.: > 200°C Elemental analysis: Anal. Calc. for $\text{C}_{24}\text{H}_{40}\text{Cl}_3\text{CoN}_9\text{O}_7$: C, 39.34; H, 5.46; N, 17.21%; Found: C, 39.33; H, 5.17; N, 17.16%. IR (KBr pellet, ν/cm^{-1}): 3288, 2911, 1616, 1592, 1429, 1326, 1235, 1182, 1001, 899, 857, 682, 587, 489, 459.

2.2c Complex 3: 0.5020 g (4.2 mmol) 5-amino-2-cyanopyridines and 40 mL anhydrous ethanol were dispersed in a 100 mL round flask, then 1.9984 g (8.4 mmol) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added into the above solution. The mixture was refluxed for 48 h (80–90°C). After hot filtration, solution was evaporated slowly in the air, and light green crystals appeared. Yield: 15%. M.p.: >200°C. Elemental analysis: Anal. Calc. for $\text{C}_{16}\text{H}_{26}\text{Cl}_2\text{NiN}_6\text{O}_4$: C, 38.74; H, 5.24; N, 16.93%; Found: C, 38.55; H, 5.41; N, 16.54%. IR (KBr pellet, ν/cm^{-1}): 3306, 3201, 1634, 1593, 1569 1470, 1420, 1385, 1363, 1310, 1287, 1206, 1162, 1045, 1018, 848, 817, 772, 672, 633, 536, 487.

2.2d Complex 4: 1.1990 g (10.0 mmol) 5-amino-2-cyanopyridines and 40 mL anhydrous ethanol were dispersed in a 100 mL round flask, then 0.9817 g (5.0 mmol) $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ was added into the above solution. The mixture was refluxed for 48 h (80–90°C). After hot filtration, solution was evaporated slowly in the air, and yellow crystals appeared. Yield: 35%. M.p.: 150–154°C. Elemental analysis: Anal. Calc. $\text{C}_{16}\text{H}_{26}\text{Cl}_2\text{MnN}_6\text{O}_4$: C, 39.04; H, 5.32; N, 17.07%; Found: C, 39.56; H, 5.53; N, 16.93%; IR (KBr pellet, ν/cm^{-1}): 3297, 3186, 2985, 2319, 1632, 1589, 1568, 1504, 1474, 1384, 1304, 1286, 1199, 1158, 1107, 1014, 904, 849, 806, 704, 666, 657, 624, 572, 529, 515, 462.

2.3 The Henry reaction catalyzed by complexes

Catalyst (0.075 mmol) was dissolved in 1 mL CH_3OH , 0.05 mL benzaldehyde (0.5 mmol) and 0.25 mL

(5 mmol) nitromethane were added to the methanol solution in a dry 25 mL Schlenk flask. The reaction mixture was stirred vigorously for 24 h at room temperature and then was analyzed by ^1H NMR.

3. Results and Discussion

3.1 Synthesis and structures

The use of 5-amino-2-cyanopyridine with 2.0 equiv of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in ethanol first resulted in the formation of 5-amino-2-ethylpyridine-2-carboximidate as the intermediate; the 1:1 adduct with CuCl_2 , 1:3 adduct with CoCl_2 , and 1:2 adduct with NiCl_2 were then obtained unexpectedly. In

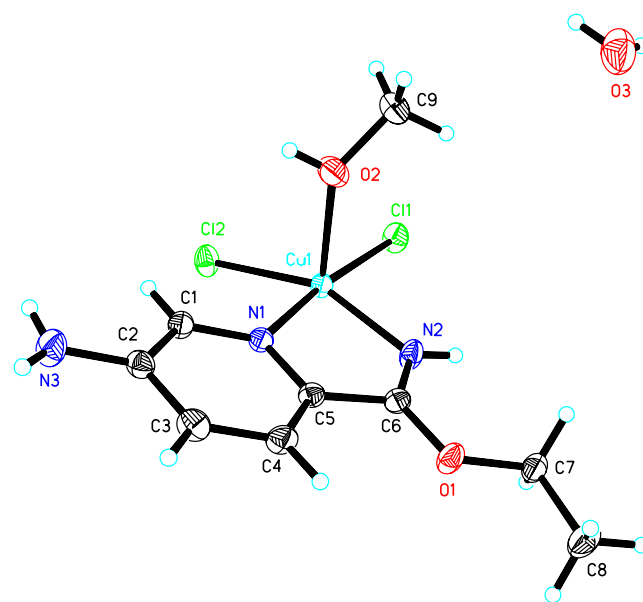


Figure 1. ORTEP diagram of complex **1** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Cu(1)–N(2) 1.960(2), Cu(1)–N(1) 2.0412(18), Cu(1)–O(2) 2.2542(18), Cu(1)–Cl(2) 2.2587(6), Cu(1)–Cl(1) 2.2833(7), N(2)–Cu(1)–N(1) 80.05(8), N(2)–Cu(1)–O(2) 100.26(9), N(1)–Cu(1)–O(2) 84.29(7), N(2)–Cu(1)–Cl(2) 155.86(7), N(1)–Cu(1)–Cl(2) 92.31(5), O(2)–Cu(1)–Cl(2) 101.73(6), N(2)–Cu(1)–Cl(1) 93.15(6), N(1)–Cu(1)–Cl(1) 173.17(5), O(2)–Cu(1)–Cl(1) 96.48(6), Cl(2)–Cu(1)–Cl(1) 94.17(2), C(1)–N(1)–Cu(1) 127.42(15), C(5)–N(1)–Cu(1) 112.97(14), C(6)–N(2)–Cu(1) 116.38(16), Cu(1)–N(2)–H(2) 122.6(19).

contrast, the synthesis of complex **4** was carried out in anhydrous ethanol using a molar ratio of 2:1 of 5-amino-2-cyanopyridine to $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; since no crystals appeared for the ligand to $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ for molar ratio of 1:2, we adopted a molar ratio of 2:1 instead of 1:2, which then afforded the yellow crystals of complex **4** after slow evaporation in air.

All the reactions were refluxed for 48 h. The crystal structures of the green complex **1** and purple red complex **2** were obtained after recrystallization in methanol, whereas the light green crystals of complex **3** were formed by slow evaporation of the filtrate of the ethanol solvent. It is noteworthy that in this reaction, the range of pH value are all between 7–8, which are weakly alkaline.

The synthetic routes for the above mentioned four complexes **1-4** can be summarized as follows (schemes 1–4, figures 1–4).

The formation of complexes **1-4** occurs through an intermediate of the functionalized $\text{CH}_3\text{CH}_2\text{OC}=\text{NH}$

group obtained from ethanol by the attack of the cyano group by the nucleophilic reagents. The complexes were all easily soluble in methanol and ethanol and dissolved with difficulty in n-hexane, petroleum ether and ether.

It is important to note that one HCl molecule was produced in the synthesis of complex **2**. Ammonium salts were formed with one of the amino groups of the tridentate ligands. In complex **2**, Co(III) may be obtained by air oxidation of Co(II) complex. And we have proved this conjecture carrying this work under anaerobic condition (N_2) isolating Co(II) complex which could be oxidized by H_2O_2 to Co(III) complex, **2**.

The structures of complexes **1-4** were determined by X-ray diffraction.

Complex **1** is a Cu-N complex with a free H_2O molecule. Cu(II) is five-coordinated with square geometry, the coordination sphere composed of two N atoms from a chelating 5-amino-O-ethyl pyridine-2-carboximidate ligand, one methanol molecule, and two chloride atoms. The bond length of Cu(1)-N(1) [2.0412

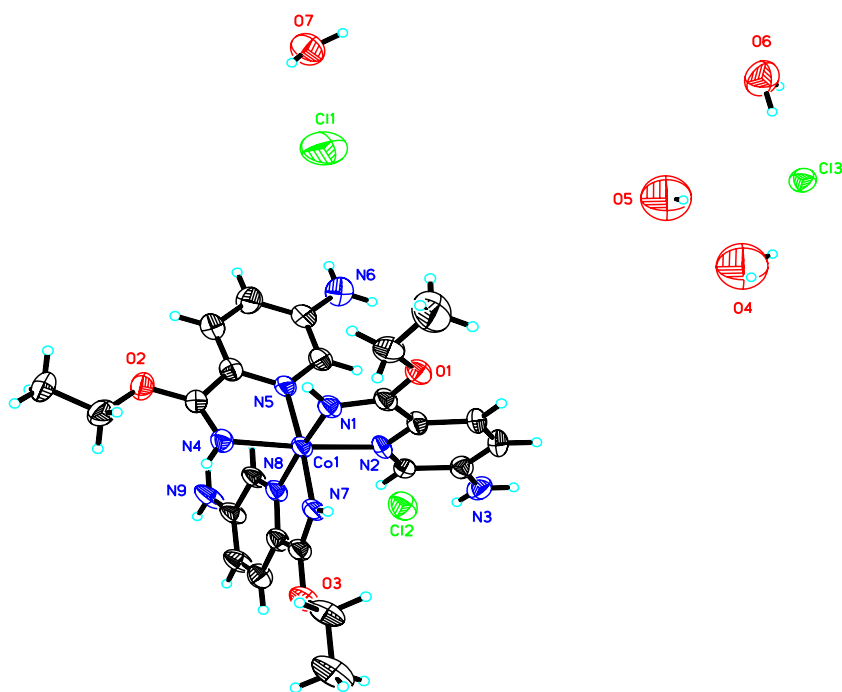


Figure 2. ORTEP diagram of complex **2** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Co(1)-N(7) 1.893(5), Co(1)-N(1) 1.910(5), Co(1)-N(4) 1.918(6), Co(1)-N(5) 1.931(6), Co(1)-N(2) 1.933(5), Co(1)-N(8) 1.940(5), N(7)-Co(1)-N(1) 92.5(2), N(7)-Co(1)-N(4) 93.2(3), N(1)-Co(1)-N(4) 92.4(2), N(7)-Co(1)-N(5) 176.3(2), N(1)-Co(1)-N(5) 89.1(2), N(4)-Co(1)-N(5) 83.4(2), N(7)-Co(1)-N(2) 89.1(2), N(1)-Co(1)-N(2) 83.1(2), N(4)-Co(1)-N(2) 175.80(2), N(5)-Co(1)-N(2) 94.4(2), N(7)-Co(1)-N(8) 82.8(2), N(1)-Co(1)-N(8) 175.3(2), N(4)-Co(1)-N(8) 88.1(2), N(5)-Co(1)-N(8) 95.6(2), N(2)-Co(1)-N(8) 96.6(2), C(1)-N(1)-Co(1) 114.7(5), C(2)-N(2)-Co(1) 112.6(5), C(9)-N(4)-Co(1) 113.7(5), C(10)-N(5)-Co(1) 113.14(4), C(14)-N(5)-Co(1) 128.3(5), C(17)-N(7)-Co(1) 115.7(4), C(22)-N(8)-Co(1) 126.4(5), C(18)-N(8)-Co(1) 112.6(4).

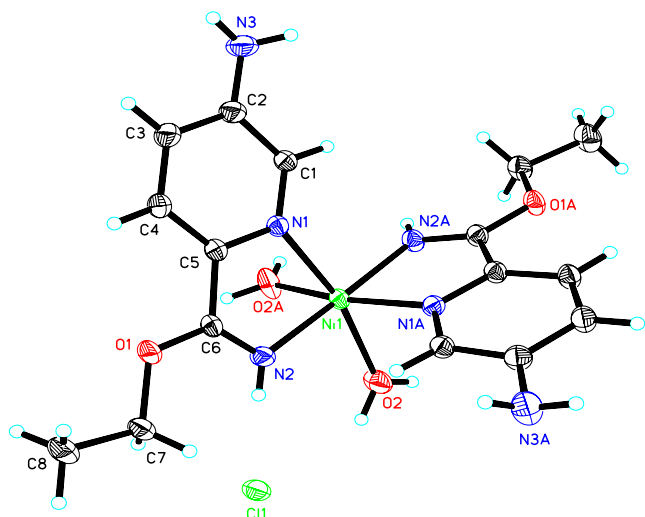


Figure 3. ORTEP diagram of complex **3** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ni(1)-O(2) 2.0925(17), Ni(1)-O(2)#1 2.0925(17), Ni(1)-N(1) 2.0902(18), Ni(1)-N(2)#1 2.040(2), Ni(1)-N(2) 2.040(2), O(2)#1-Ni(1)-O(2) 90.38 (11), N(1)#1-Ni(1)-O(2) 87.72(8), N(1)-Ni(1)-O(2) 167.09(6), N(1)#1-Ni(1)-O(2)#1 167.09(6), N(1)-Ni(1)-O(2)#1 87.72(8), N(1)-Ni(1)-N(1)#1 96.89(10), N(2)#1-Ni(1)-O(2)#1 88.86(7), N(2)#1-Ni(1)-O(2) 94.83(8), N(2)-Ni(1)-O(2) 88.86(7), N(2)-Ni(1)-O(2)#1 94.83(8), N(2)-Ni(1)-N(1)#1 97.90(8), N(2)#1-Ni(1)-N(1) 97.90(8), N(2)#1-Ni(1)-N(1)#1 78.58(7), N(2)-Ni(1)-N(1) 78.58(7), C(1)-N(1)-Ni(1) 126.86(15), C(5)-N(1)-Ni(1) 113.54(14), C(6)-N(2)-Ni(1) 116.26(15).

(18) Å] is longer than the bond length of Cu(1)-N(2) [1.960 (2) Å], which are consistent with the values previously reported for five coordinated mononuclear Cu complex such as Dichloro(O-ethyl 3-methylpyridine-2-carboximidic acid- k^2N,N')copper(II).¹² The crystal structure of complex **1** is stabilized by numerous hydrogen bonds of O-H \cdots Cl, N-H \cdots Cl, O-H \cdots O, and N-H \cdots O.

Complex **2** is a Co-N complex. The central cobalt ion (Co²⁺) shows a nearly octahedral six-fold coordination and is surrounded by three N (pyridine) atoms and by three (imino ether group) donor atoms in the facial configuration. The complex consists of [Co(EtPy)₃]²⁺ cations, Cl⁻ counter-anions and two H₂O molecules. EtPy is an N, N-coordinated bidentate ligand. The Co-N bond lengths range from 1.893 (5) Å to 1.940 (5) Å, which are in agreement with the literature without unusual features.¹⁰ The N(7)-Co(1)-N(8) and N(4)-Co(1)-N(2) angles were 82.8 (2)° and 175.8 (2)°, respectively, and other N-Co(1)-N angles were in the range, 83.1 (2)°–175.3 (2)°.

The crystal structures of complexes **3** and **4** are similar, with both showing a symmetric structure and six-fold coordination consisting of [Ni(5-amino-EtPy)₂]²⁻ anions or [Mn(5-amino-EtPy)₂]²⁻ anions, Cl⁻ counter

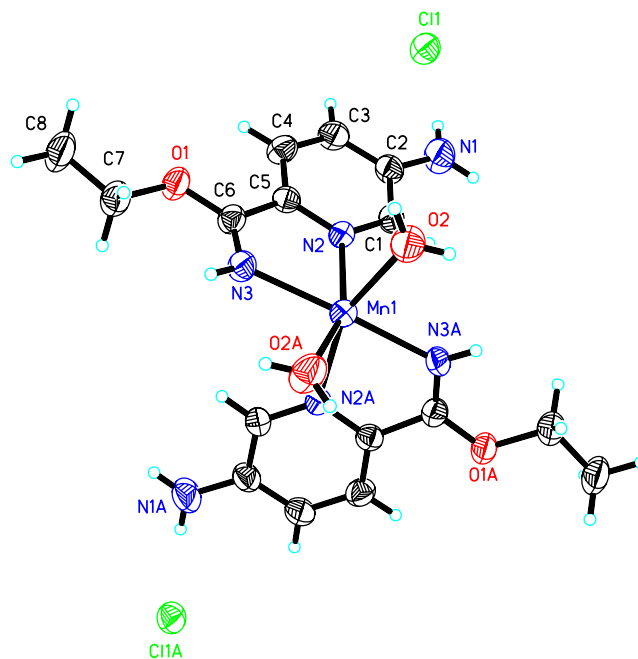


Figure 4. ORTEP diagram of complex **4** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mn(1)-O(2) 2.167(4), Mn(1)-O(2)#1 2.167(4), Mn(1)-N(3)#1 2.191(5), Mn(1)-N(3) 2.191(5), Mn(1)-N(2)#1 2.282 (4), Mn(1)-N(2) 2.282(4), O(2)-Mn(1)-O(2)#1 92.3(2), O(2)-Mn(1)-N(3)#1 86.43(17), O(2)#1-Mn(1)-N(3)#1 104.66 (16), O(2)-Mn(1)-N(3) 104.66(16), O(2)#1-Mn(1)-N(3) 86.42 (17), N(3)#1-Mn(1)-N(3) 164.2(3), O(2)-Mn(1)-N(2)#1 157.98(14), O(2)#1-Mn(1)-N(2)#1 89.18(16), N(3)#1-Mn(1)-N(2)#1 71.98(17), N(3)-Mn(1)-N(2)#1 97.36(16), O(2)-Mn(1)-N(2) 89.17(16), O(2)#1-Mn(1)-N(2) 157.98(14), N(3)#1-Mn(1)-N(2) 97.36(16), N(3)-Mn(1)-N(2) 71.98(17), N(2)#1-Mn(1)-N(2) 97.62(19), C(1)-N(2)-Mn(1) 125.5(3), C(5)-N(2)-Mn(1) 115.2(3), C(6)-N(3)-Mn(1) 119.7(4).

anions and two H₂O molecules. All atoms are in the same general positions. The nitrogen atom is surrounded by two O atoms (H₂O molecules) and by four N (5-amino-2-cyanopyridine) atoms. The Ni(1)-O(2), Ni(1)-N(1) and Ni(1)-N(2) bond lengths are 2.0925(17), 2.0902 (18) Å, and 2.040 (2) Å, respectively. The N(1)-Ni(1)-O(2), N(2)-Ni(1)-O(2), N(2)-Ni(1)-N(1) bond angles are 167.09(6)°, 88.86(7)°, and 78.58(7)°, respectively. The Mn-N bond lengths range from 2.1915 (5) Å to 2.282 (5) Å. Both the Mn-N and Ni-N are in agreement with those reported for Di- μ -acetato-bis(dimethylformamide)pentakis(μ -N,2-dioxidobenzene-1-carboximidato)tetrakis(1-ethylimidazole)pentamanganese(III)manganese(II)-diethylether-dimethylformamide-methanol-water^{13,14} and [Ni(O-methylpyridine-2-carboximidate)₃]Br₂·4H₂O.¹⁰

These structural parameters are all typical. Such values are usually found for the combinations of such free molecules with complexes formed by hydrogen bonds.

3.2 Henry Reactions

Henry reaction (table 1) was catalyzed by 15 mol% of the four complexes **1-4** without any additives in methanol. The catalytic activities are shown in table 1.

Inspection of the data in table 1 shows that the conversion efficiency of these complexes were higher than 55%. Further optimization reactions were explored at room temperature with lower catalyst loadings of 10 mol% and 5 mol%. We were delighted to observe that the complexes **1-4** in methanol at room temperature afforded the corresponding nitroalcohol with 10 mol% after 24 h in 74%, 68%, 78%, respectively, and 42%, but afforded the corresponding nitroalcohol in 17%, 66%, 68% and 29% when the catalyst loading is reduced to 5 mol% (table 2).

We also did a parallel experiment without the catalysts, and the conversion efficiency was only 26%. It is much lower than that of the Henry reaction with complexes as catalysts.

From the tables 1 and 2, we can conclude that all complexes were effective catalysts for the Henry

reaction, and complex **3** (15 mol%) was found to be the best choice for this reaction, giving 87% conversion.

The following catalytic reaction mechanism can be proposed: the complexes first strongly activate the C=O bond, which is followed by nucleophilic addition reaction of CH_2NO_2^- onto the carbonyl group.

4. Conclusions

In conclusion, the crystal structures of four metal complexes involving 5-amino-2-ethylpyridine-2-carboximidate have been reported for the first time. The complexes were synthesized using a simple method. The obtained complexes were shown to be good catalysts for the Henry reaction. Further study of these complexes in other organic reactions such as cyanosilylation and hydroboration reactions is currently ongoing.

Supplementary Information (SI)

Crystallographic information for all the compounds have been deposited with the Cambridge crystallographic data center, (CCDC) as supplementary publications CCDC 1455248, 1455249, 1455251 and 1455252. The electronic Supplementary Information is available at www.ias.ac.in/chemsci.

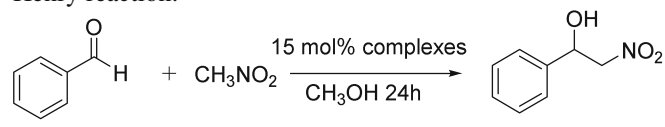
Acknowledgments

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Table 1. Catalytic activity of the four complexes to the Henry reaction.^a



Complex	Conversion (%) ^b
1	67
2	83
3	87
4	55
no catalysts	26

^aReactions were carried out with 0.5 mmol PhCHO and 0.25 mL CH_3NO_2 in 1 mL CH_3OH using 15 mol% of catalyst at room temperature (10–20°C). ^bConv.% was determined by ^1H NMR.

Table 2. Effect of the catalysts loading to the Henry reaction.^a

Complex	Conversion (%) ^{b,c}	Conversion (%) ^{b,d}
1	74	17
2	68	66
3	78	68
4	42	29

^aReactions were carried out with 0.5 mmol PhCHO and 0.25 mL CH_3NO_2 in 1 mL CH_3OH using 10 mol% of catalyst at room temperature (10–20°C). ^bConversion % was determined by ^1H NMR. ^c10 mol% catalyst loading. ^d5 mol% catalyst loading.