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Synthesis and catalytic activity of novel Zn–N and Cu–N complexes

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The Henry reaction

ABSTRACT

A series of zinc and copper complexes supported by 1, 3-diaminobenzene, 1, 2-aminobenzylamine, 1, 3-aminobenzylamine and m-xylylenediamine was synthesized and characterized. Reaction of 1, 3-diaminobenzene, 1, 2-aminobenzylamine, 1, 3-aminobenzylamine and m-xylylenediamine with $Zn(OAc)_2 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ in alcohol, methanol or tetrahydrofuran resulted in the production of five novel zinc and copper complexes: **2**, **4**, **6**, **8** and **9**. Moreover, the structure of each of complex was determined by X-ray diffraction analysis. Every complex was also characterized by elemental analysis, ^1H NMR and IR. The complexes were then used to catalyze the Henry reaction and good catalytic results (65–99%) were achieved. The catalytic activity of the complexes was determined by ^1H NMR.

Many novel zinc complexes and copper complexes have been reported recently [1–12]. Metal complexes are the subject of intensive research not only owing to their rich coordination chemistry but also to a number of established and potential application areas. Metal-complexes occupy an important position in catalytic processes, as the catalysts and they have shown high activities in organic reactions and polymerization. Recently, organometallic complexes including Zn, Cu (Zn, Li), Fe, Ru and other less-frequently used ions have been developed. These complexes have been used in selective 1,2- or 1,4-additions, transfer hydrogenations, aldol reactions and Diels–Alder reactions [13]. For example, N, O-chelated aluminum and zinc complexes are active catalysts in the ring-opening polymerization of ε-caprolactone [14]. Chiral Phosphoramide–Zn (II) complexes are highly active catalysts for enantioselective organozinc addition to ketones [15]. Cu(II)-containing MOFs based on N-heterocyclic ligands are widely used in the oxidative coupling of 2,6-dimethylphenol [15]. In this paper, we first describe the synthesis of novel complexes with a simple, one-pot method. On the complex **9**, in 2001 and 2002, Hamerton, Ian research group reported the preparation, characterization, and storage behavior of transition metal–diamine complexes as the curing agents for epoxy resins [16,17], but we first report herein the definite crystal structure of complex **9**. In recent years, it has been reported in the literature that chiral nitrogen and zinc as well as copper and nitrogen complexes have showed high activity in the Henry reaction [16–22]. Inspired by their work, our complexes were used to catalyze the Henry reaction.

The synthetic routes of the title five complexes can be summarized as follows (Schemes 1–4, Figs. 1–5).

The syntheses of the complexes **2**, **4** and **6** were all carried out under anhydrous ethanol, using a ratio of 1.1:1 of the ligand to the zinc acetate. After refluxing for 24 h, complex **2** was recrystallized with dichloromethane and n-hexane (V/V: 1/1), and brown crystals were obtained. Complex **4** was recrystallized with ethanol, and colorless crystals were obtained. By adding 10 mL dichloromethane and 10 mL n-hexane (v/v:1/1), complex **6** was evaporated slowly in the air, and colorless crystals appeared.

The synthesis of complex **8** was carried out under anhydrous methanol, first refluxed 8 h at a 1:1 ratio, then a second volume of ligand, equal to the first, was added, and the reaction was refluxed for an additional 8 h. Next, the product mixture was evaporated in ethanol, and blue crystals were obtained.

The synthesis of complexes **8** and **9** was carried out under THF using a ratio of 2:1 of the ligand to the zinc acetate or copper acetate. Both reactions were refluxed for 24 h. Complex **9** was obtained after slow evaporation in the ethanol.

The crystal structures of complexes **8** and **9** are distinctive. Complex **8** also contains an acetic acid molecule with a freed root, which is similar to the structure of complex **9**.

The five complexes were all easily dissolved in dichloromethane, chloroform, ethanol and methanol, and were difficult to dissolve in n-hexane, petroleum ether and ether.

The coordination number was 4 for complexes **2**, **4**, **6**, 3 for complex **8** and 5 for complex **9**. Complex **2** was a $[Zn\ (C_6H_8N_2)\ (OAc)_2]$

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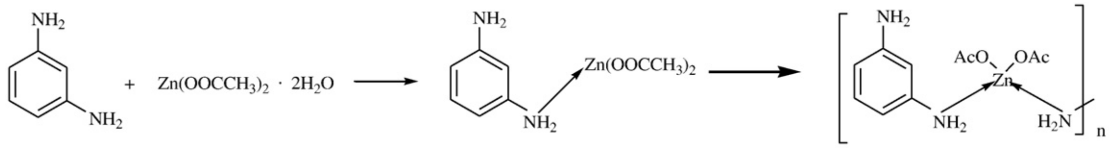
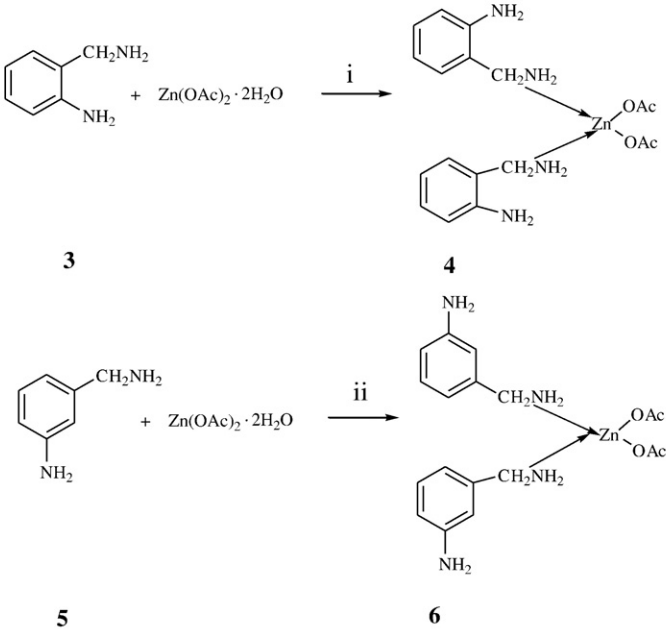


1 **2**

Scheme 1. The synthetic route for complex **2**[a]. [a]Reagents and conditions: (i) ethanol, 70–80 °C, 24 h; (ii) ethanol, 70–80 °C, 24 h.



Scheme 2. The synthetic route for complexes **4** and **6**[a]. [a]Reagents and conditions: (i) ethanol, 70–80 °C, 24 h; (ii) ethanol, 70–80 °C, 24 h.

unit consisting of polymer complexes [Zn $(C_6H_8N_2)$ $(OAc)_2]_n$, which was an unlimited extension of its chain structure. The carboxylate oxygen atoms (O1 and O3) and the nitrogen atoms N1, N2 of phenylenediamine constitute the four atoms coordinated to Zn.

Complex **4** consisted of a Zn $(OAc)_2$ molecule and two 1, 2-aminobenzylamine molecules. The Zn ion was coordinated with the carboxylate oxygen atoms O1 and O1i and the 1, 2-aminobenzylamine nitrogen atoms N1 and N1i forming a four-coordinated complex.

Similarly, Complex **6** single also consisted of a Zn $(OAc)_2$ molecules and two 1, 2-aminobenzylamine molecules. The Zn ion was coordinated with carboxylate oxygen atoms O1 and O3 and with aminobenzylamine nitrogen atoms N2 and N4, thus forming a four-coordinate complex.

Complex **8** was a Cu–N complex that consisted of a Cu $(OAc)_2$ molecule and two m-xylylenediamine molecules. A Cu ion was complexed with a carboxylate oxygen atom (O1) and the two m-xylylenediamine nitrogen atoms N1, N2, N3 and N4; this, the complex was three coordinate.

Complex **9** was a Cu–N complex that consisted of a $Cu(OAc)_2$ molecule and two 1,2-aminobenzylamine molecules. A Cu ion was complexed with a carboxylate oxygen atom (O1) and the aminobenzylamine nitrogen atoms N1, N2, N3 and N4, thus making the complex five coordinate, The Cu1–O1 bond length [1.9939 (15) Å] and the Cu1–N2 and Cu1–N3 bond lengths were slightly longer than the Cu1–N1 and Cu1–N4 bond lengths.

Catalyze the Henry reaction was achieved using 15 mol% of the six complexes without any additives. The catalytic activity of the five novel complexes in the Henry reaction was shown in Table 1.

From Table 1, we can see that the conversion efficiency for each of these complexes was more than 60%, they are all good catalysts to the Henry reaction. Among them, complex **6** showed the best catalytic activity. The mechanism can be proposed that the complexes could greatly activate the C O bond, followed by nucleophilic addition reaction of $CH_2NO_2^-$ onto the carbonyl group.

In conclusion, five novel complexes were synthesized with a simple, one-pot method, and their crystal structures were determined. Further research on the use of these complexes in other organic reactions such as the cyanosilylation reaction and allylation is ongoing.

Acknowledgment

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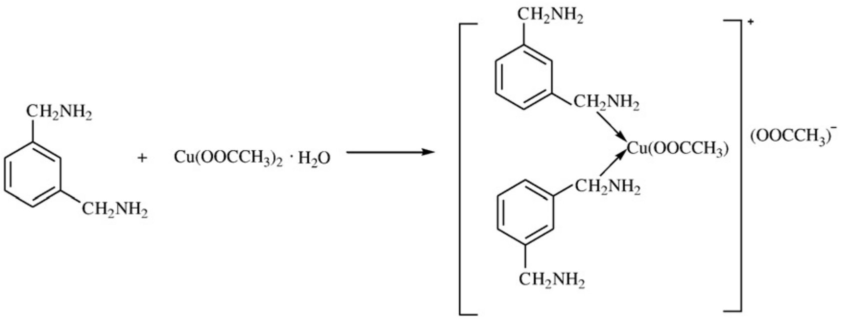
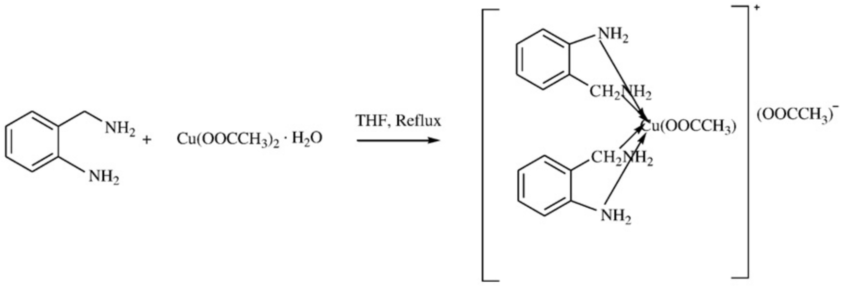
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.05.017.



7 **8**

Scheme 3. The synthetic route for complex **8**[a]. [a]Reagents and conditions: (i) methanol, 60–70 °C, 16 h.



3 **9**

Scheme 4. The synthetic route for complex **9**^{a}. ^{a}Reagents and conditions: THF, 60–70 °C, 24 h.

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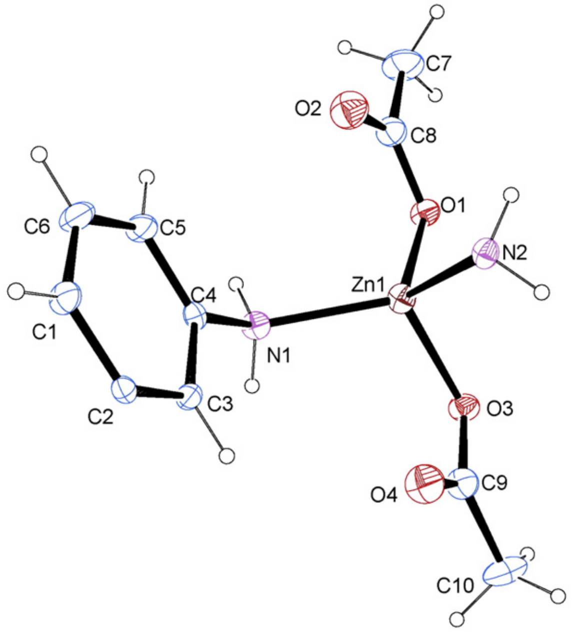


Fig. 1. ORTEP diagram of complex **2** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Zn(1)–O(1) 2.006(3), Zn(1)–O(3) 2.001(3), Zn(1) –N(1) 2.038(4), Zn(1)–N(2) 2.032(4), O(1)–C(8) 1.281(5), O(2)–C(8) 1.222(5), O(3)–C(9) 1.275(5), O(4)–C(9) 1.235(5), N(1)–C(4) 1.4385, N(2)–C(2) 1.436(5), O(1)–Zn(1)–O (3) 92.28(12), O(1)–Zn(1)–N(1) 107.72(13), O(1)–Zn(1)–N(2) 109.76(13), O(3)–Zn (1)–N(2) 110.77(14), O(3)–Zn(1)–N(1) 107.89(14), N(2)–Zn(1)–N(1) 123.83(14), C (8)–O(1)–Zn(1) 109.9(3), C(9)–O(3)–Zn(1) 108.8(3), C(4)–N(1)–Zn(1) 120.9(3), C (2)–N(2)–Zn(1),117.5(3). Elemental analysis: Anal. Calc. for Zn[$C_{10}H_{14}N_2O_4$]: C, 41.19; H, 4.839; N, 9.607%; Found: C, 41.50; H, 4.976; N, 9.799%. ^{1}H NMR (300 MHz,$CDCl_3$, 27 °C): δ(ppm) = 6.93 (t, 1H), 6.11–6.12 (d, J = 6.5 Hz, 2H), 6.04(s, 1H), 3.82(s,4H), 2.11(s, 6H), IR (KBr, pellet):3434, 3219,3143, 3013, 2975, 2923, 2365, 1632, 1615, 1587, 1505, 1483, 1424, 1387, 1335, 1320, 1206, 1192, 1149, 1125, 1052, 1038, 1019, 950, 930, 859, 773, 675, 619, 585, 553, 540, 442.

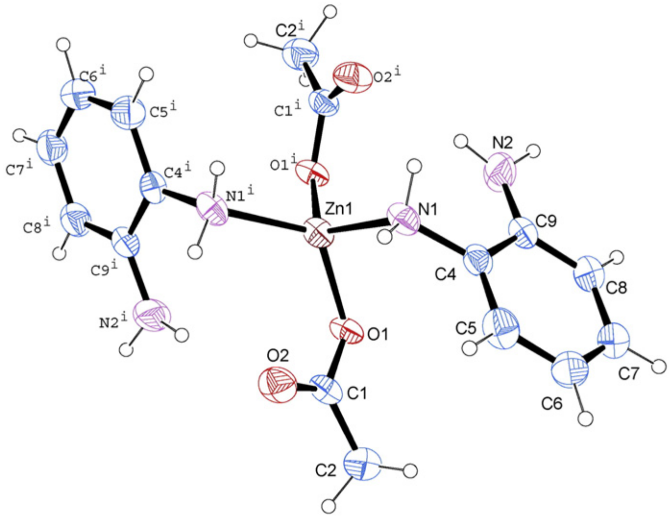


Fig. 2. ORTEP diagram of complex **4** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Zn(1)–O(1) 1.953(5), Zn(1)–N(1) 2.019(5), O(1)–C(8) 1.279(7), O(2)–C(8) 1.220(8), N(1)–C(1) 1.496(7), N(2)–C(3) 1.381(9), C(8)–C(9) 1.484(9), C(1)–C(2) 1.502(7),O(1)–Zn(1)–N(1) 120.5(2), C(1)–C(2)–C(3) 120.6(5), N (1)–Zn(1)–N(1i) 107.0(3), Zn(1)–O(1)–C(8) 118.5(5), Zn1–N(1)–C(1)115.5(4), N(1)–C(1)–C(2) 112.4(5), N(2)–C(3)–C(2) 120.9(6), N(2)–C(3)–C(4) 120.9(5), O(1)–C(8)–O(2) 121.5(6), O(1)–C(8)–C(9) 116.1(6), O(2)–C(8)–C(9) 122.4(6), C(1)–C(2)–C(7) 120.7(5). Elemental analysis: Anal. Calc. for Zn[$C_9H_{13}N_2O_2$]2: C, 50.53; H, 6.13; N, 13.10%. Anal. Calc. for Zn[$C_9H_{13}N_2O_2$]$_2$:Found:C, 50.74; H, 6.208; N, 13.11%. ^{1}H NMR (300 MHz,$CDCl_3$, 27 °C), δ(ppm) = 7.10–7.29(m, 4H), 6.80–6.89 (m, 4H), 3.99 (s, 4H),1.96 (s, 6H),1.89(br, 8H), IR (KBr, pellet):3852, 3738, 3431, 3303, 3245, 2931,1613, 1587, 1494, 1391, 1337, 1275, 1158, 1023, 977, 937, 865, 743, 624, 580, 494.

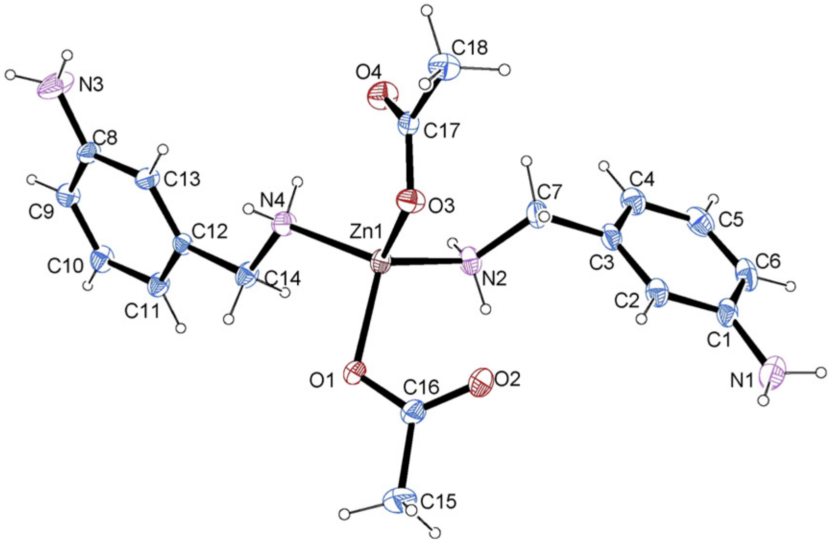


Fig. 3. ORTEP diagram of complex **6** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Zn(1)–O(1) 1.9618(19), Zn(1)–O(3) 1.9722(19), Zn(1)–N(4) 2.019(2), Zn(1)–N(2) 2.036(2), O(1)–C(16) 1.253(4), O(2)–C(16) 1.228(3), O(3)–C(17) 1.277(3), O(4)–C(17) 1.225(3), N(1)–C(1) 1.387(5), N(2)–C(7) 1.472(3), N(3)–C(8) 1.366(4), N(4)–C(14) 1.439(3), C(3)–C(7) 1.506(4), C(12)–C(14) 1.513(4), O(1)–Zn1–N(2) 108.7(9), O(1)–Zn1–N(4) 102.95(9), O(1)–Zn1–O(3) 110.29(9), O(3)–Zn1–N(2) 109.76(8), O(3)–Zn1–N(4) 114.72(10), N(2)–Zn1–N(4) 110.10(11), Zn1–O(1)–C(16) 112.81(19), Zn1–O(3)–C(17) 112.89(17), Zn1–N(2)–C(7) 113.93(15), Zn1–N(4)–C(14) 118.66(19), N(1)–C(1)–C(6) 122.3(4), N(1)–C(1)–C(2) 119.6(4), N(3)–C(8)–C(9) 120.7(3), N(3)–C(8)–C(13) 120.7(3), N(4)–C(14)–C(12) 117.5(3). Elemental analysis: Anal. Calc. for Zn$[C_9H_{13}N_2O_2]_2$: C, 50.53; H, 6.13; N, 13.10%; Found: C, 50.31; H, 6.15; N, 13.32%. ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): δ(ppm) = 7.11 (t, J = 0.5 Hz, 2H), 6.58–6.65 (m, 6H), 3.76(s, 4H), 2.2(s, 8H), 2.00(s, 6H), IR (KBr pellet): 3430, 3320, 3230, 2950, 2360, 2140, 1590, 1400, 1330, 1140, 1010, 781, 679, 623, 476.

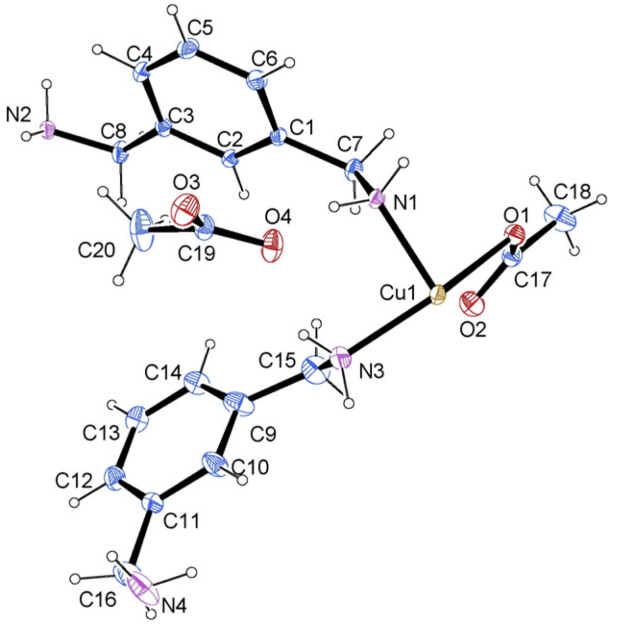


Fig. 4. ORTEP diagram of complex **8** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Cu(1)–N(1) 2.026(3), Cu(1)–N(2) 2.031(3), Cu(1)–O(1) 2.034(3), O(3)–C19 1.230(6),O(2)–C(17) 1.239(6), O(4)–C(19) 1.250(6), N(3)–C(15) 1.388(8), N(4)–C(16) 1.357(8), N(1)–Cu(1)–O(1) 86.29(13), N(2)–Cu(1)–O(1) 92.58(13), N(1)–Cu(1)–N(3) 90.79(16), N(2)–Cu(1)–N(3) 90.90(16), O(1)–Cu(1)–N(3) 149.63(16), N(1)–Cu(1)–N(4)87.09(15), N(2)–Cu(1)–N(4)92.18(16), O(1)–Cu(1)–N(4) 117.25(19), N(3)–Cu(1)–N(4) 92.7(2), C(17)–O(1)–Cu(1) 108.7(3), C(7)–N(1)–Cu(1) 117.4(3), O(2)–C(17)–O(1) 122.6(4),O(2)–C(17)–C(18) 120.3(4), O(1)–C(17)–C(18) 117.1(4). Elemental analysis: Anal. Calc. for $C_{20}H_{30}N_4O_4Cu$: C, 52.91; H, 6.66; N, 12.34%; Found: C, 52.54; H, 6.78; N, 13.33%. IR (KBr pellet): 3334, 3219, 2926, 2878, 1571, 1444, 1401, 1332, 1174, 1158, 1090, 1055, 993, 926, 919, 791, 755, 734,703, 651,639, 616.

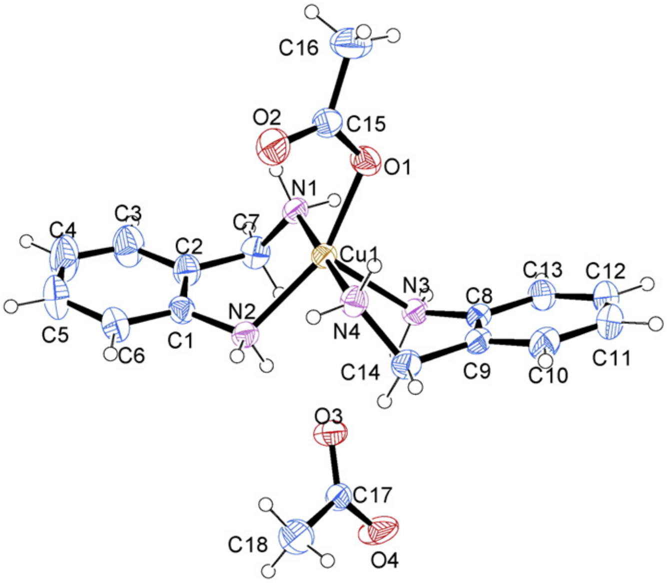
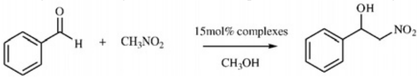


Fig. 5. ORTEP diagram of complex **9** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Cu(1)–N(1) 1.9843(17), Cu(1)–O(1) 1.9939(15), Cu(1)–N(4) 2.0153(17), Cu(1)–N(2)2.1205(17), Cu(1)–N(3)2.2846(16), O(3)–C17 1.253(3), O(1)–C(15) 1.267(3), N(3)–C(8) 1.422(3), N(4)–C(14) 1.484(3), N(1)–C(7) 1.471(3), O(4)–C(17) 1.225(3), N(2)–C(1) 1.433(3), O(2)–C(15)1.227(3), N(1)–Cu(1)–O(1) 86.76(7), N(1)–Cu(1)–N(4) 177.54(7), O(1)–Cu(1)–N(4) 91.42(7), N(1)–Cu(1)–N(2) 91.01(7), O(1)–Cu(1)–N(2) 157.23(6), N(4)–Cu(1)–N(2)90.02(7), N(1)–Cu(1)–N(3) 92.84(6), O(1)–Cu(1)–N(3) 103.69(6), N(4)–Cu(1)–N(3) 89.20(6), N(2)–Cu(1)–N(3) 99.06(6), C(15)–O(1)–Cu(1) 114.36(13), C(8)–N(3)–Cu(1) 113.67(12), C(14)–N(4)–Cu(1) 116.57(13), C(7)–N(1)–Cu(1) 116.37(14),C(1)–N(2)–Cu(1) 115.04(13), Anal. Calc. for Cu$[C_9H_{13}N_2O_2]_2$: C, 50.70; H, 6.10; N, 13.15%. Found: C, 50.55; H, 6.43; N, 13.38%, IR (KBr pellet): 3451, 3342, 3230, 3183, 3113, 3067, 3028, 2950, 2886, 2349, 1576, 1496, 1468, 1454, 1418, 1394, 1334, 1279, 1223, 1159, 1121, 1087, 1041, 1020, 995, 945, 860, 846, 754, 664, 650, 623, 587, 492, 472.

Table 1

Catalytic activity of the six complexes to the Henry reaction[a].



Complex	Conversion (%)[b]
2	63
4	67
6	>99
8	69
9	67

[a] Reactions were carried out with 1 mmol PhCHO and 0.2 mL CH_3NO_2 in 5 mL CH_3OH using 15 mol% of catalysts at room temperature (10–20 °C).

[b] Conv.% was determined by ^1H NMR.