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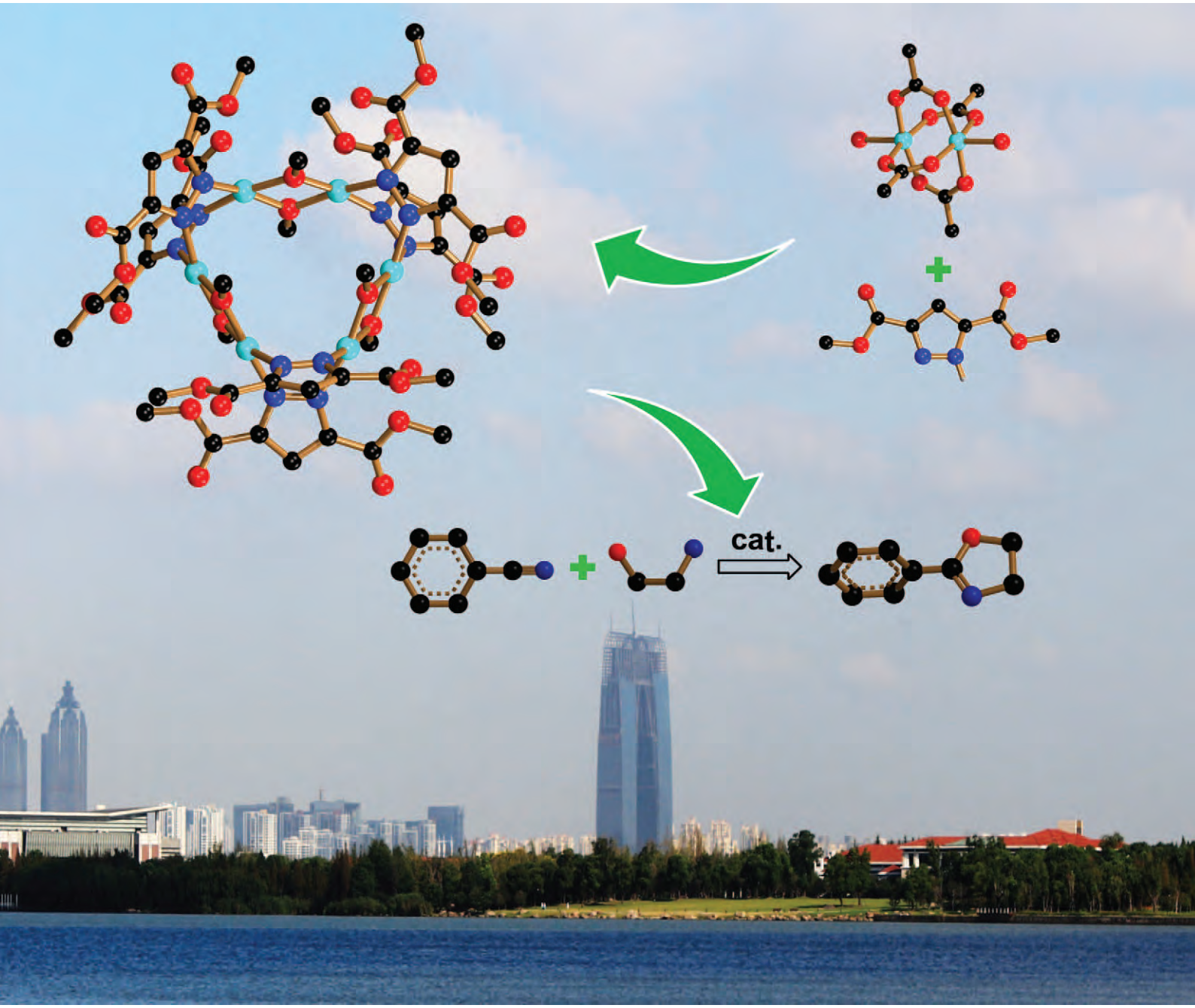

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Polynuclear copper(II) pyrazolate complexes: temperature-dependent protonolysis reactions, crystal structures and high catalytic activity toward the condensation of nitriles with 2-aminoalcohol†

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Reaction of $Cu(OAc)_2{\cdot}H_2O$ and 1*H*-pyrazole-3,5-dicarboxylic acid dimethyl ester (Hdcmpz) in MeOH at room temperature afforded one tetranuclear Cu(II)/pyrazolate complex $[\{Cu_2(\mu\text{-}OAc)_2\}_2(\mu\text{-}dcmpz)_2(\mu\text{-}OAc)_2]$ (**1**) in 89% yield. The similar reaction in refluxing MeOH produced a hexanuclear metallamacrocyclic Cu(II)/pyrazolate complex $[\{Cu(\mu\text{-}dcmpz)\}_2(\mu\text{-}OMe)_2]_3$ (**2**) in 85% yield. Treatment of the same components under solvothermal conditions resulted in the formation of another tetranuclear Cu(II)/pyrazolate/carboxylate complex $[\{Cu(MeOH)\}_4(\mu\text{-}mcccpz)_4]$ (**3**, Hmcccpz = 5(3)-(methoxycarbonyl)-1*H*-pyrazole-3(5)-carboxylic acid) in 30% yield. The $mcccpz^{2-}$ ion in **3** was *in situ* generated *via* the hydrolysis of one of two esters on dcmpz ligand. Complexes **1–3** were characterized by elemental analysis, IR and single-crystal X-ray diffraction. An X-ray analysis revealed that **1** contains two $\{Cu(\mu\text{-}OAc)\}_2$ fragments that are interconnected by two $\mu\text{-}\eta^2,\eta^2\text{-}dcmpz^-$ ligands and two $\mu\text{-}\eta^1,\eta^1\text{-}OAc^-$ ions, forming a unique tetrameric structure. Complex **2** is composed of three $\{Cu(\mu\text{-}dcmpz)\}_2$ fragments linked by three pairs of $\mu\text{-}OMe^-$ anions, forming a metallamacrocyclic crown structure. **3** consists of four {Cu(MeOH)} fragments linked by two pairs of $\mu\text{-}\eta^1,\eta^2\text{-}mcccpz^{2-}$ ligands, forming a tetrameric [2 × 2] grid-like structure. Complexes **1–3** displayed high catalytic activity toward the condensation of nitriles with 2-aminoalcohol under solvent-free conditions to produce various 2-oxazolines.

Introduction

In the past few decades, copper pyrazolate complexes have been extensively studied due to their structural chemistry and their potential applications in magnetism, luminescence, and catalysis.[1] The anion of pyrazole is well suited for its coordination to copper ions *via* the *N*,*N*′-bridging mode. The structures of the copper pyrazolate complexes ranged from di-,[2] tri-,[3] tetra-, penta-,[2a,c,4] hexa-,[5] polynuclear[6] structures to chains, layers,[7] or three-dimensional networks.[8] These complexes were mostly prepared by direct reactions of Cu(I)/(II) ions with pyrazole ligands in the presence of bases,[2a,5a,c] or oxidation reactions of Cu(I) pyrazolates,[5e,6c,d,8f] or self-assembly reactions from preformed copper pyrazolates,[2a–c,5e] or solvothermal reactions of copper salts with pyrazole.[6b,7a,b,8a–c] However, another approach, protonolysis reactions of Cu(II) carboxylates with the derivatives of pyrazole, has been less explored to synthesize copper pyrazolates. This may be due to the fact that such ligands could not serve as suitable precursors for protonolysis as carboxylic acids may have a stronger acidity.[4f,9] For example, reaction of $Cu(OAc)_2$ with pyrazole (Hpz) afforded one trinuclear Cu(II)/pyrazolate complex $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(OAc)_2(Hpz)]$, in which part of the OAc^- anions in $Cu(OAc)_2$ was protonolysed by Hpz ligand.[9a] However, the analogous reactions of $Cu(OAc)_2$ with some substituted pyrazoles such as 4-methyl-1*H*-pyrazole (4-MepzH), 3,5-dimethyl-1*H*-pyrazole (3,5-Me_2pzH), 3,4,5-trimethyl-1*H*-pyrazole (3,4,5-Me_3pzH) and 3-methyl-4-phenyl-1*H*-pyrazole (3-Me-4-PhpzH) only yielded the corresponding undeprotonated products $[Cu(OAc)_2(L)_2]$ (L = 4-MepzH, 3,5-Me_2pzH, 3,4,5-Me_3pzH, 3-Me-4-PhpzH).[9a] When the pyrazole ligand was designed to have some chelating groups on the pyrazolyl ring, their protonolysis reactions with acetates could proceed. For instance, mixing $Cu(OAc)_2$ and 3,5-bis-

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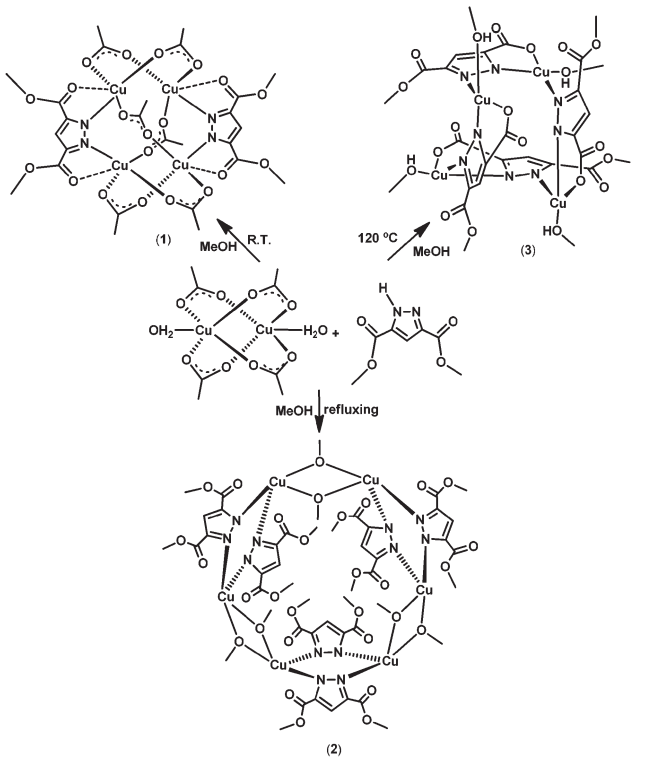
(2,6-diisopropylphenyliminoacetyl)-1*H*-4-methylpyrazole (Hbsippiampz) with chelating side arms on the pyrazolyl ring resulted in the formation of a deprotonated product [(bsippiampz)$_2$Cu$_6$(μ-OAc)$_6$(μ$_4$-O)$_2$].[9c] Could other pyrazole ligands with substituent groups attached on the pyrazolyl ring promote such protonolysis reactions? We deliberately chose another pyrazole derivative, 1*H*-pyrazole-3,5-dicarboxylic acid dimethyl ester (Hdcmpz) that possesses two –COOMe groups on the 3 and 5 positions on its pyrazolyl group based on the following considerations. Firstly, the electron-withdrawing ester groups on the pyrazolyl ring, which enhances the acidity of the pyrazole ligand, may initiate the protonolysis reaction. Secondly, the ester group COOMe is not a good O-donor species but could weakly coordinate at Cu(II) centers,[1f,10a] which may work as potential catalytic sites for some organic substrates. Thirdly, copper(II) ion could catalyze the *in situ* hydrolysis of the ester group into carboxylate anion, which in turn binds Cu(II) centers to generate new Cu(II)/carboxylate complexes.[1f,10b] In addition, it was found that solvothermal reaction of Cu(OAc)$_2$ with 3,5-Me$_2$pzH gave rise to the trimeric complex [Cu(3,5-Me$_2$pz)]$_3$, in which all OAc$^-$ anions could be protonolysed by 3,5-Me$_2$pzH ligands.[10c] Thus another question was raised: could the reaction temperatures affect the protonolysis of the pyrazole ligand with acetate anion and the structures of the resulting Cu(II)/pyrazolate complexes? Bearing these questions in mind, we carried out the reactions of Cu(OAc)$_2$·H$_2$O with Hdcmpz in MeOH at three different reaction temperatures, and isolated one tetranuclear and one hexanuclear Cu(II)/pyrazolate complexes [{Cu$_2$(μ-OAc)$_2$}$_2$(μ-dcmpz)$_2$(μ-OAc)$_2$] (**1**) and [{Cu(μ-dcmpz)}$_2$(μ-OMe)$_2$]$_3$ (**2**) and one tetranuclear Cu(II)/pyrazolate/carboxylate complex [{Cu(MeOH)}$_4$(μ-mcccpz)$_4$] (**3**, Hmcccpz = 5(3)-(methoxycarbonyl)-1*H*-pyrazole-3(5)-carboxylic acid). In all cases, the protonolysis of Hdcmpz with OAc$^-$ anion did occur and in **3**, one of two esters on the dcmpz$^-$ ligand was *in situ* hydrolyzed into the mcccpz^{2-} anion.

On the other hand, 2-oxazolines are ubiquitous in biochemical, biological, and medicinal structures and functions.[11] These 2-oxazolines could be prepared through the cyclodehydration of hydroxyl amides,[11b,c] or the condensation of carboxylic acids,[12] esters,[13] nitriles,[14] *N*-acylbenzotriazoles,[15] or aldehydes[16] with amino alcohols. Recently, transition metal catalysts such as molybdenum oxide,[17] RuCl$_2$(PPh$_3$)$_2$,[18] and tungstophosphoric acid[14] were also employed to catalyze these reactions. However, their catalytic reactions have some potential limitations because the transformations generally suffered from poor functional group tolerance, elevated reaction temperatures, low product yields, or using expensive catalysts and environmentally unfriendly solvents. To this end, the development of cheaper copper catalysts under solvent-free conditions for such tandem reactions would be necessary. Several groups[6c,19–22] have found that copper pyrazolates exhibit high reactivity in many organic transformations, including C–N bond formation,[19] oxidation of alkane,[20] cyclopropanation of olefins,[9a,21] and polymerization of MMA.[22] In this paper, complexes **1–3** were employed to efficiently catalyze the condensation of nitriles with 2-aminoalcohol under solvent-free conditions to generate various 2-oxazolines. Their syntheses, crystal structures and catalytic properties are described below.

Results and discussion

Synthetic and spectral aspects

As shown Scheme 1, reactions of Cu(OAc)$_2$·H$_2$O with two equiv. of Hdcmpz in MeOH at room temperature, did not afford the expected 1 : 2 product 'Cu(dcmpz)$_2$', but a tetracopper pyrazolate complex [{Cu$_2$(μ-OAc)$_2$}$_2$(μ-dcmpz)$_2$(μ-OAc)$_2$] (**1**) in 89% yield. Compound **1** was the only product isolated regardless of the Cu(OAc)$_2$·H$_2$O/Hdcmpz molar ratios. It is noted that the acetates in Cu(OAc)$_2$·H$_2$O were partially protonolysed by Hdcmpz ligand, which may be due to the facts that the electron-withdrawing ester groups on the pyrazolyl ring may enhance the acidity of Hdcmpz ligand. If the reaction temperature was raised, could all the acetates in Cu(OAc)$_2$·H$_2$O be replaced by dcmpz$^-$ anions to form 1 : 2 product 'Cu(dcmpz)$_2$'? When the methanol solution containing Cu(OAc)$_2$·H$_2$O and two equiv. of Hdcmpz was refluxed for 6 h, one hexanuclear copper(II) pyrazolate complex [{Cu(μ-dcmpz)}$_2$(μ-OMe)$_2$]$_3$ (**2**) was isolated in 85% yield. In this reaction, half of the OAc$^-$ anions in Cu(OAc)$_2$·H$_2$O were protonolysed by Hdcmpz ligands while the others were protonolysed by MeOH molecules. To explore the temperature effect further, we ran the reaction of Cu(OAc)$_2$·H$_2$O and Hdcmpz in MeOH at 120 °C under solvothermal conditions to produce blue



Scheme 1 Syntheses of complexes **1–3** at three different temperatures.

octahedral crystals of $[\{Cu(MeOH)\}_4(\mu\text{-mcccpz})_4]\cdot 4MeOH\cdot 0.5H_2O$ ($\mathbf{3}\cdot 4MeOH\cdot 0.5H_2O$) in 30% yield. In this reaction, one of two COOMe groups of Hdcmpz was *in situ* hydrolyzed into a carboxylate group, forming a new mcccpz^{2-} ligand. All the OAc$^-$ anions in $Cu(OAc)_2$ were removed from the Cu(II) centers and replaced by two N atoms of the deprotonated pyrazolyl groups and one O atom of the carboxylate group of the mcccpz^{2-} ligand. Attempts to run the same reactions at 150 °C or higher temperatures always led to the formation of an unidentified precipitate that is insoluble in common solvents. To our knowledge, it is uncommon that three different Cu(II)/pyrazolate complexes were generated from the same components *via* controlling the reaction temperatures. Complexes **1–3** are stable toward oxygen and moisture. They are insoluble in toluene, hexane, Et_2O, but soluble in DMSO and DMF. Their elemental analyses were consistent with their chemical formula. In the FT-IR spectra of **1–3**, the strong peaks at 1710/1687 cm^{-1} (**1**), 1711/1687 cm^{-1} (**2**) and 1694/1628 cm^{-1} (**3**) were assigned to be the carboxylate stretching vibrations. The bands at 1508/1487 cm^{-1} (**1**), 1512/1469 cm^{-1} (**2**), 1516/1489 cm^{-1} (**3**) were assigned as the C=N stretching vibrations of dcmpz$^-$ (**1** and **2**) or mcccpz^{2-} (**3**) ligand. Their identities were finally confirmed by X-ray crystallography. Powder X-ray diffraction was employed to confirm the bulk phase homogeneity of the three complexes. For **1–3**, the measured PXRD patterns are closely matched with the simulated patterns generated from the results of single crystal X-ray diffraction data (ESI, Fig. S3–S5†). As shown in the TGA curve of **3** (ESI, Fig. S6†), the weight loss of 12.50% in the range of 35–120 °C was ascribed to the removal of all coordinated MeOH molecules. TGA curves revealed that **1–3** were similar and began to decompose upon 200 °C.

Crystal structure of $\mathbf{1\cdot 3CH_2Cl_2}$. Compound $\mathbf{1}\cdot 3CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit contains the discrete molecule $[\{Cu_2(\mu\text{-OAc})_2\}_2(\mu\text{-dcmpz})_2(\mu\text{-OAc})_2]$ and three CH_2Cl_2 solvent molecules. Compound **1** may be viewed as having a tetrahedral structure, in which two $\{Cu(\mu\text{-}\eta^1,\eta^1\text{-OAc})\}_2$ units are connected by two $\mu\text{-}\eta^2,\eta^2$-dcmpz$^-$ ligands (Fig. 1). And the four Cu(II) centers are further bridged by a pair of decussate $\mu\text{-}\eta^1,\eta^1$-OAc$^-$ anions. Judged from the bond angles listed in Table 1, Cu(1) or Cu(2) in **1** can be described as having a square pyramidal coordination geometry in which O(14), O(16), O(17), and N(1) (or O(11), O(9), O(20), and N(2)) atoms sit on the basal plane while O(1) (or O(3)) atom from the COOMe group occupies the apical position. While Cu(3) and Cu(4) atoms adopt a distorted trigonal bipyramidal coordination geometry, coordinated by one N and one O atoms of dcmpz ligand and three O atoms from three bridging OAc$^-$ anions. In **1**, the Cu–O(AcO) bond lengths (1.919(3) Å–1.973(3) Å) are longer than the Cu–O(C=O) bond lengths (2.368(3) Å–2.670(3) Å). The mean Cu–O(AcO) bond length of 1.948(3) Å is comparable to that of the corresponding one in $[Cu_3(\mu_3\text{-OH})(\mu\text{-pz})_3(AcO)_2(Hpz)]$ (1.962(2) Å).[9a] The Cu(1)–N (2.001(3) Å) and Cu(2)–N (1.997(3) Å) bond lengths are slightly longer than Cu(3)–N (1.958(3) Å) and Cu(4)–N (1.955(3) Å) bond lengths, which may be due to their different coordination geometries. The Cu(1)···Cu(2) (4.115(2) Å) and Cu(3)···Cu(4) (3.736(2) Å) separations bridged by the dcmpz ligand are much longer than the Cu(2)···Cu(3) (3.220(2) Å) and Cu(4)···Cu(1) (3.180(2) Å) contacts bridged by a pair of OAc$^-$ anions.

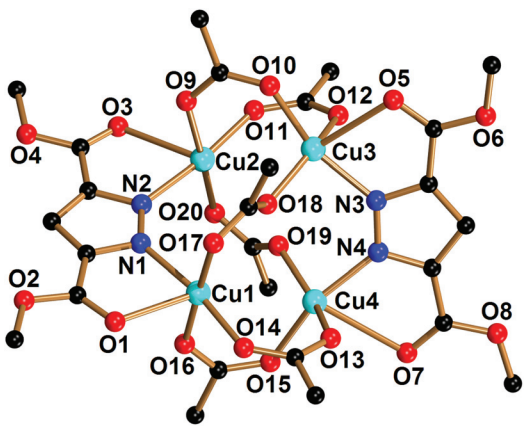


Fig. 1 View of the molecular structure of **1** with a labelling scheme. All hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) for **1–3**[a]

Compound **1**			
Cu(1)–O(14)	1.940(3)	Cu(1)–O(16)	1.950(3)
Cu(1)–O(17)	1.973(3)	Cu(1)–N(1)	2.001(3)
Cu(2)–O(11)	1.943(3)	Cu(2)–O(9)	1.958(3)
Cu(2)–O(20)	1.969(3)	Cu(2)–N(2)	1.997(3)
Cu(3)–O(10)	1.919(3)	Cu(3)–O(18)	1.943(3)
Cu(3)–O(12)	1.958(3)	Cu(3)–N(3)	1.958(3)
Cu(4)–O(15)	1.921(3)	Cu(4)–O(19)	1.950(3)
Cu(4)–O(13)	1.953(3)	Cu(4)–N(4)	1.955(3)
Cu(1)–O(1)	2.368(3)	Cu(2)–O(3)	2.448(3)
Cu(3)–O(5)	2.525(3)	Cu(4)–O(5)	2.670(3)
Cu(1)···Cu(2)	4.115(2)	Cu(2)···Cu(3)	3.220(2)
Cu(3)···Cu(4)	3.736(2)	Cu(4)···Cu(1)	3.180(2)
Compound **2**			
Cu(1)–O(29)	1.9026(11)	Cu(1)–O(30)	1.9088(16)
Cu(1)–N(3)	1.9911(19)	Cu(1)–N(1)	1.9918(14)
Cu(2)–O(10)	1.9011(14)	Cu(2)–O(9)	1.9022(13)
Cu(2)–N(4)	1.9720(16)	Cu(2)–N(2)	1.9817(15)
Cu(3)–O(9)	1.9094(14)	Cu(3)–O(10)	1.9127(12)
Cu(3)–N(5)	1.9644(17)	Cu(3)–N(7)	1.9807(15)
Cu(4)–O(20)	1.9098(14)	Cu(4)–O(19)	1.9194(12)
Cu(4)–N(6)	1.9678(14)	Cu(4)–N(8)	1.9831(18)
Cu(5)–O(19)	1.9098(14)	Cu(5)–O(20)	1.9106(12)
Cu(5)–N(9)	1.9677(16)	Cu(5)–N(11)	1.9832(14)
Cu(6)–O(30)	1.9162(11)	Cu(6)–O(29)	1.9168(16)
Cu(6)–N(12)	1.9651(13)	Cu(6)–N(10)	1.9894(18)
Cu(1)–O(5)	2.736(2)	Cu(2)–O(3)	2.641(2)
Cu(3)–O(15)	2.862(2)	Cu(4)–O(17)	2.812(2)
Cu(5)–O(21)	2.802(2)	Cu(6)–O(28)	2.942(2)
Cu(1)···Cu(6)	3.0087(9)	Cu(1)···Cu(2)	3.1383(8)
Cu(2)···Cu(3)	2.9907(7)	Cu(3)···Cu(4)	3.172(1)
Cu(4)···Cu(5)	3.101(8)	Cu(5)···Cu(6)	3.1818(8)
Compound **3**			
Cu(1)–O(3A)	1.947(3)	Cu(1)–N(2A)	1.953(4)
Cu(1)–N(1)	1.972(4)	Cu(1)–O(5)	1.983(3)
Cu(1)–O(1)	2.436(3)	Cu(1)···Cu(1A)	4.1160(6)

[a] Symmetry code: (A) $1.0 - x$, $1.5 - y$, $2.0 + z$ for **3**.

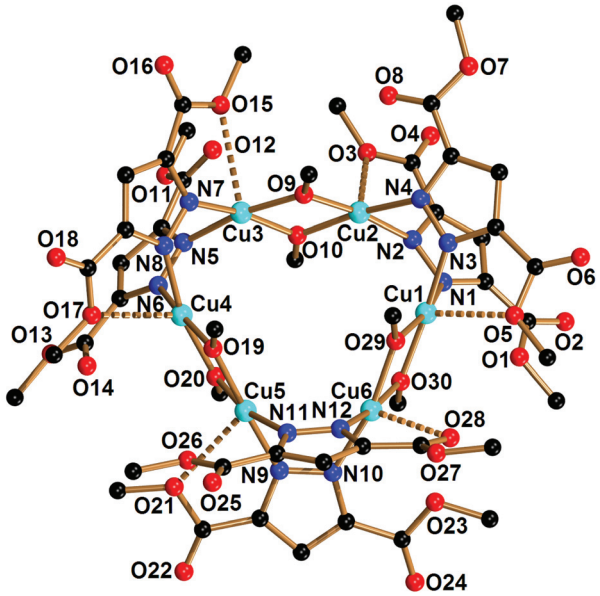


Fig. 2 View of the molecular structure of **2** with a labelling scheme. All hydrogen atoms are omitted for clarity.

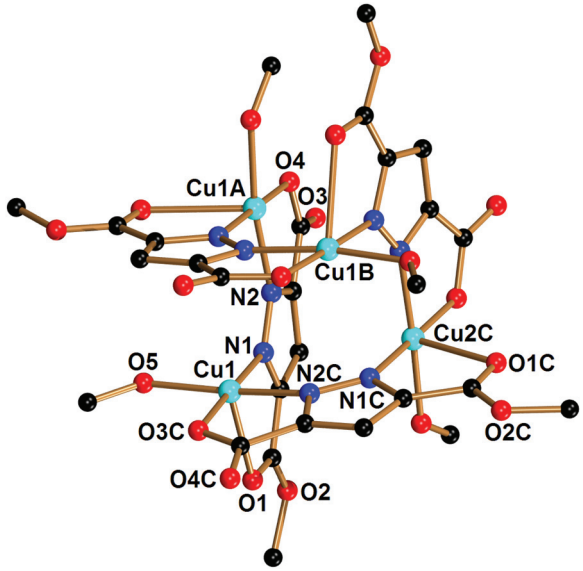


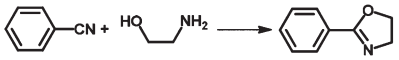
Fig. 3 View of the molecular structure of **3** with a labelling scheme. All hydrogen atoms are omitted for clarity. Symmetry codes: A, $-y + 3/4, x + 3/4, -z + 3/4$; B, $-x, -y + 3/2, z$; C, $y - 3/4, -x + 3/4, -z + 3/4$.

Crystal structure of 2. Compound **2** crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit consists of the independent molecule $[\{Cu(\mu\text{-dcmpz})\}_2(\mu\text{-OMe})_2]_3$. Complex **2** consists of three $\{Cu(\mu\text{-OMe})\}_2$ units linked by three pairs of $\mu\text{-}\eta^1,\eta^1$-dcmpz anions, forming a metallamacrocyclic crown structure with an approximate D_{3h} symmetry (Fig. 2). Such a crown structure was observed in some known hexanuclear complexes [*cis*-$Cu_6(\mu\text{-OH})_6(\mu\text{-pz})_6$],[6b] $[Au(PPh_3)_2][$*trans*-$Cu_6(\mu\text{-OH})_6\{\mu\text{-}(3,5\text{-}CF_3)_2pz\}_6X]$ (X = Cl, Br, I).[5e] However, the connection modes between Cu(II) atoms in these complexes are somewhat different. In **2**, the three $[Cu_2(\mu\text{-OMe})_2]$ fragments approximately locate in a plane while three pairs of dcmpz ligands stand above or below the Cu_6 plane. While each Cu center in [*cis*-$Cu_6(\mu\text{-OH})_6(\mu\text{-pz})_6$] and the anion of $[Au(PPh_3)_2][$*trans*-$Cu_6(\mu\text{-OH})_6\{\mu\text{-}(3,5\text{-}CF_3)_2pz\}_6X]$ (X = Cl, Br, I) is interlinked by one pyrazolate and one hydroxyl ligands with its neighboring Cu(II) ions. In **2**, each Cu(II) atom has a distorted square planar geometry, coordinated by two OMe^- and two $dcmpz^-$ ligands to form a four-membered Cu_2O_2 ring and one six-membered Cu_2N_4 ring. The Cu···Cu contacts of 3.1383(8)–3.1818(8) Å in Cu_2N_4 rings are longer than the corresponding ones in Cu_2O_2 rings (2.9907(7)–3.101(8) Å) (Table 1). The Cu(1)–O(5), Cu(2)–O(3), Cu(3)–O(15), Cu(4)–O(17), Cu(5)–O(21), and Cu(6)–O(28) bond distances are relatively long (2.641(2) Å–2.942(2) Å), indicating that the O atoms of C=O groups on $dcmpz^-$ ligand interact only weakly with the Cu(II) centers. The mean Cu–N bond length (1.978(2) Å) is consistent with that in **1**. The mean Cu–μ-O(OMe) bond length (1.910(2) Å) in **2** is shorter than that observed in $[Cu_7(\mu_3\text{-OH})_4(\mu\text{-OCH}_3)_2(\mu\text{-L})_6]\text{-}Cl_2\cdot x CH_2Cl_2$ (1.935(4) Å and 2.176(4) Å; HL = 3-pyridyl-5-*tert*-butylpyrazole).[6f]

Crystal structure of 3·4MeOH·0.5H$_2$O. Compound **3**·4MeOH·0.5H_2O crystallizes in the tetragonal space group $I4_1/a$, and its asymmetric unit contains one fourth of the discrete molecule $[\{Cu(MeOH)\}_4(\mu\text{-mcccpz})_4]$ and one MeOH and one water molecules. In **3**, four [Cu(MeOH)] fragments are connected by four $mcccpz^{2-}$ ligands through two nitrogen and one oxygen atoms, forming a tetranuclear [2 × 2] grid-type structure with a S_4 symmetry (Fig. 3). Such a framework resembles those of complexes $[\{Cu(H_2O)\}_4(\mu\text{-mcccpz})_4]$,[4h] $[M_4(HL1)_4]$ (M = Cu(II), Ni(II); H_3L1 = *N*,*N*′-bis(2-pyridylmethyl)pyrazole-3,5-dicarboxamide),[4h] $[Cu_4L2_6\text{-}(DMF)_2][PF_6]_2$ (HL2 = 3-(2-pyridyl)pyrazole) and $[Cu_4L3_4(DMF)_4][PF_6]_4$ (HL3 = 6-(3-pyrazolyl)-2,2A-bipyridine).[4f] The Cu···Cu contacts in **3** are 4.1160(6) Å, and 4.3811(6) Å, which are too long to include any metal–metal interaction. The four Cu(II) atoms are located on the vertices of a distorted tetrahedron with the Cu–Cu–Cu angles of 64.309(11)° and 57.846(11)°, where the four short edges are spanned by four $mcccpz^{2-}$ ligands. In the structure of **3**, each Cu center is coordinated by two N atoms and two O atoms of two $mcccpz^{2-}$ ligand, and one MeOH molecule to form a square pyramidal coordination geometry. The O(5), O(3C), N(2C) and N(1) atoms surrounding Cu(1) atom sit on the basal plane while the O(1) atom from the COOMe group of $mcccpz^{2-}$ ligands is located on the axial position. The mean Cu–N bond distance of 1.962(4) Å is shorter than those in **1** and **2** (Table 1). The Cu–O(COOMe) (2.436(3) Å) bond length is much longer than the Cu–O(COO) bond distance (1.947(3) Å) and the Cu–O(MeOH) bond distance (1.983(3) Å), suggesting weak coordination of COOMe group at Cu(II) centers in **3**.

Synthesis of 2-oxazolines catalyzed by 1–3. As discussed above, copper(II) ions in **1–3** weakly interact with the COOMe groups, COO^- anions, MeOH molecules or OMe^- anions, which may be easily replaced by organic substrates. Thus complexes **1–3** may exhibit catalytic activity toward some organic transformations. To explore the catalytic activities of **1–3**

Table 2 Optimizing the reaction conditions for the synthesis of 2-phenyloxazoline



Entry	Cat.	Catalyst loading ([Cu] (mol %))	Temp (°C)	Time (h)	Benzonitrile : aminoalcohol	Yield[a] (%)
1	**1**	8	80	6	1 : 3	63
2	**2**	8	80	6	1 : 3	65
3	**3**	8	80	6	1 : 3	67
4	**1**	8	20	6	1 : 3	—
5	**1**	8	40	6	1 : 3	—
6	**1**	8	60	6	1 : 3	2
7	**1**	8	100	6	1 : 3	85
8	**1**	8	120	6	1 : 3	50
9	**1**	8	100	6	1 : 1	18
10	**1**	8	100	6	1 : 2	33
11	**1**	8	100	6	1 : 4	90
12	**1**	8	100	6	1 : 5	89
13	**1**	4	100	6	1 : 4	47
14	**1**	6	100	6	1 : 4	59
15	**1**	10	100	6	1 : 4	88
16	**1**	12	100	6	1 : 4	90
17	**1**	8	100	2	1 : 4	36
18	**1**	8	100	4	1 : 4	85
19	**1**	8	100	8	1 : 4	59
20	—	—	100	6	1 : 4	38

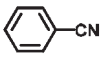
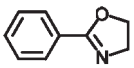
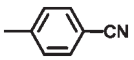
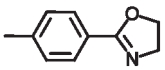
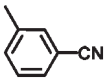
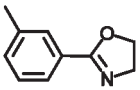
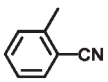
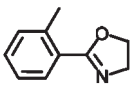
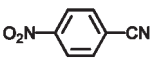
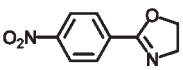
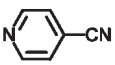
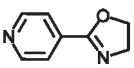
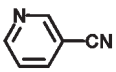
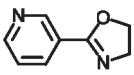
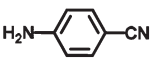
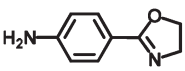
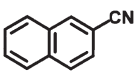
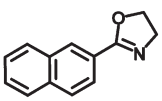
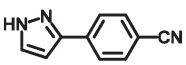
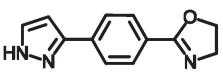
[a] Isolated yield.

toward the condensation reaction of nitriles with aminoalcohol, each catalyst (2.0 mol% (**1**), 1.33 mol% (**2**), 2.0 mol% (**3**)) was mixed with benzonitrile (1.0 mmol), and 2-aminoalcohol (3.0 mmol) at 80 °C for 6 h. A standard workup produced 2-phenyloxazoline in 63%, 65%, and 67% yield, respectively (Table 2, entries 1–3). These preliminary results showed that the tandem reaction between nitrile and 2-aminoalcohol could be efficiently catalyzed by **1–3**.

As shown in Table 2, benzonitrile and 2-aminoalcohol were chosen as the model substrates to optimize the reaction conditions including reaction temperature, catalyst loading, and the ratio of benzonitrile to 2-aminoalcohol. The reaction temperature usually exerts great impact on such a reaction. At lower temperature (20 °C to 60 °C), the reaction did not work (entries 4 and 5) or gave the product in a very low yield (entry 6). When the reaction temperature was raised to 80 °C or 100 °C, the product yields could be raised to 63% and 85%, respectively (entries 1 and 7). While the yield of the resulting 2-phenyloxazoline became only 50% as the temperature was raised up to 120 °C (entry 8). To optimize the molar ratio of benzonitrile to 2-aminoalcohol, several ratios (1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5) were employed. As shown in Table 2, the ratio of benzonitrile to 2-aminoalcohol imposed important effects on the yield of 2-phenyloxazoline. The yield of 2-phenyloxazoline was gradually increased from 18% to 90% as the ratio of benzonitrile to 2-aminoalcohol was raised from 1 : 1 to 1 : 4 (entries 1 and 9–11) at 100 °C. Furthermore, the catalyst loading may also affect the catalytic activity to some extent. The product yield was gradually increased from 47% to 90% as the ratio of benzonitrile to **1** was raised from 100 : 1 to 200 : 1 (entries 11, 13 and 14). The reaction time can influence the catalytic activity. To optimize the time interval, several different time intervals (2, 4, 6, and 8 h) were employed while keeping the other reaction conditions unchanged. As shown in Table 2, while the time interval was raised, the yield of 2-phenyloxazoline increased in the forepart, and then that decreased after 6 h. It is noteworthy that the reaction was not able to proceed smoothly without using a catalyst, giving only a low yield (38%).

Upon the above optimization, the optimal reaction conditions were identified as follows: **1** or **2**, **3**, solvent-free, 1 : 4 molar ratio of nitriles to 2-aminoalcohol and with a reaction temperature of 100 °C. With the optimized reaction conditions in hand, a variety of substituted nitrile derivatives were chosen as the substrates in this tandem reaction. As shown in Table 3, the condensation reactions were performed well for all the substrates examined, and the desired products were isolated in moderate to excellent yields. To our delight, aromatic nitriles substituted with functional groups such as NH_2, NO_2, pyrazole were tolerated without eroding the product yields (Table 3, entries 5, 8 and 10). The reaction of nitriles bearing heterocycles (such as isonicotinonitrile, nicotinonitrile) or 2-naphthonitrile performed significantly well to give good yields (entries 6, 7 and 9). It seemed that 4-substituents of the benzene ring did not hamper the condensation reaction (entry 2). However, this reaction was sensitive to the 3- and 2-substituent of the benzene ring and good or moderate yields were obtained for 3-methylbenzonitrile (70–74% yield; entry 3) and 2-methylbenzonitrile (38–45% yield; entry 4), which may be ascribed to the steric hindrance during the course of the condensation reaction. As shown in entries 5 and 8, electron-deficient *p*-substituted aromatic nitriles were found to proceed

Table 3 Synthesis of 2-oxazolines catalyzed by **1–3**[a]

Entry	Nitrile	Product	Yield[b] (%)		
			1	**2**	**3**
1			90	93	95
2			85	90	92
3			74	70	77
4			38	41	45
5			91	94	96
6			88	86	89
7			81	79	84
8			47	46	48
9			77	76	80
10			53	56	58

[a] Reaction conditions: nitrile (1.0 mmol), 2-aminoalcohol (4.0 mmol), and catalyst loading = 8 mol% [Cu] at 100 °C for 6 h. [b] Isolated yield.

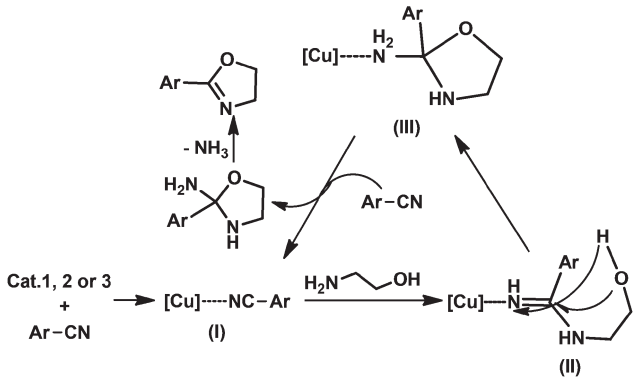
Table 4 Comparison of efficiency of various catalysts in the synthesis of 2-phenyloxazoline

Entry	Catalyst[a]	Solvent	Temperature	Time	Addition	Yield (%)
1	**1**	—	100 °C	6 h	—	90
2	**2**	—	100 °C	6 h	—	93
3	**3**	—	100 °C	6 h	—	95
4	$Cu(OAc)_2{\cdot}H_2O$	—	100 °C	6 h	—	82
5	$CuL1_2{\cdot}H_2O$	—	100 °C	6 h	NaOAc	83[11a]
6	$Cd(OAc)_2{\cdot}2H_2O$	—	130 °C	20 h	—	92[23a]
7	$Cd(OAc)_2{\cdot}2H_2O$	PhCl	130 °C	26 h	—	89[23b]
8	$ZnCl_2$	PhCl	100–130 °C	25 h	—	72[23c]
9	$ZrOCl_2{\cdot}8H_2O$	—	100 °C	5 h	—	90[24a]
10	SiO_2–TPA	—	100 °C	3 h	—	90[24b]

[a] L1 = methacrylate; TPA = 12-tungstophosphoric acid.

in higher yields than those with electron-donating substituent groups. For example, higher yield (entry 5) was obtained for 4-nitrobenzonitrile bearing electron-withdrawing substituent group relative to those of electron-donating ones (entries 8–10).

As shown in Table 3, complex **3** exhibited more efficient catalytic performance on the condensation of nitriles with 2-aminoalcohol than **1** and **2**, which may be due to the steric hindrance caused by two bulky COOMe groups on the dcmpz ligands in **1** and **2**. Table 4 lists a comparison of the results for



Scheme 2 The possible Cu(II)-catalyzed mechanism for the synthesis of 2-oxazolines.

the condensation reaction of benzonitrile with 2-aminoalcohol using different catalysts. Comparative run with $Cu(OAc)_2{\cdot}H_2O$ under the same reaction conditions indicated that **1–3** exhibited better catalytic performance as the yields (90–95%) of the resulting 2-phenyloxazoline obtained by **1–3** are higher than that (82%) obtained by $Cu(OAc)_2{\cdot}H_2O$ (Table 4, entries 1–4). The catalytic activities of **1–3** were also higher than that of cupric methacrylate complex in the presence of NaOAc.[11a] Comparing with $ZnCl_2$,[23c] $Cd(OAc)_2{\cdot}2H_2O$[23a,b] catalysts (Table 4, entries 6–8), complexes **1–3** showed a higher conversion in a shorter time at lower reaction temperatures. In the cases of entries 9 and 10 (Table 4), two catalysts ($ZrOCl_2{\cdot}8H_2O$[24a] and 12-tungstophosphoric acid (TPA) supposed by SiO_2[24b]) showed comparable catalytic activities on the condensation reaction of benzonitrile with 2-aminoalcohol than those of **1–3**. As described earlier in this article, **1** and **2** were obtained by reactions of $Cu(OAc)_2{\cdot}H_2O$ with Hdcmpz in MeOH at room temperature or in refluxing MeOH while reactions of $Cu(OAc)_2{\cdot}H_2O$ with Hdcmpz in MeOH at 120 °C produced **3**, which may indicate that **3** is more stable than **1** and **2** in solution. Thus the frameworks of **1** and **2** may not be retained under our catalytic conditions (100 °C) because they could not be recycled for further use.

The possible catalytic reaction mechanism[11a] for the above reactions is proposed as follows (Scheme 2). Firstly, the nitrile molecule replaces the COOMe group or MeOH molecule and binds at the Cu(II) center of **1–3**, producing the intermediate I. Secondly, the intermediate I may combine 2-aminoalcohol to give the intermediate II through the nucleophilic addition. Thirdly, the intermediate II may undergo intramolecular cycloaddition to generate III. Thirdly, the intermediate III may eliminate the tandem reaction product that loses one equivalent of NH_3, producing the 2-oxazoline and thus furnishing the catalytic cycle.

Conclusions

In this paper, we have demonstrated that the reactions of $Cu(OAc)_2{\cdot}H_2O$ with Hdcmpz in MeOH at three different reaction temperatures generated one tetranuclear Cu(II)/pyrazolate complex **1**, one hexanuclear Cu(II)/pyrazolate complex **2**, and one tetranuclear Cu(II)/pyrazolate/carboxylate complex **3**. In these three cases, the protonolysis of Hdcmpz with OAc^- anion took place, and especially one of two esters on the $dcmpz^-$ ligand in **3** was *in situ* hydrolyzed into the $mcccpz^{2-}$ anion. It is rare that three Cu(II)/pyrazolate complexes with different structures could be isolated from the same components *via* controlling the reaction temperature. Because the COOMe groups, COO^- anions, MeOH molecules or OMe^- anions in **1–3** interact weakly with the Cu(II) centers, and are readily replaced by organic substrates, complexes **1–3** displayed high catalytic activity toward the condensation of nitriles with 2-aminoalcohol under solvent-free conditions to produce the corresponding 2-oxazolines with high yields. It is anticipated that this synthetic methodology reported here could be applied in the rational design and assembly of other Cu(II)/pyrazolate complexes with new structures and higher catalytic activities. Studies in this respect are underway in our laboratory.

Experimental section

General procedures

All reagents were used as purchased from commercial sources without further purification. Hdcmpz[25] and 4-(1*H*-pyrazol-3-yl)-benzonitrile[26] were prepared according to the published procedures. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Varian UNITYplus-300 spectrometer. Elemental analyses for C, H, and N were performed on a Carlo-Erbo CHNO-S microanalyzer. The IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000–400 cm^{-1}). High-resolution mass spectra were obtained by using a Microma GCT-TOF instrument. The uncorrected melting points were measured on a Mel-Temo II apparatus. The powder X-ray diffraction (PXRD) measurements were carried out on a PANalytical X'Pert PRO MPD system (PW3040/60). Thermal analysis was performed with a Perkin Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} and a flow rate of 100 cm^3 min^{-1} (N_2).

$[\{Cu_2(\mu\text{-}OAc)_2\}_2(\mu\text{-}dcmpz)_2(\mu\text{-}OAc)_2]{\cdot}3CH_2Cl_2$ (**1**·3CH_2Cl_2)

To a MeOH (10 mL) solution of $Cu(OAc)_2{\cdot}H_2O$ (203 mg, 1.0 mmol) was added a MeOH solution of Hdcmpz (372 mg, 2.0 mmol). The mixture was stirred overnight at ambient temperature to form a blue precipitate. After filtration, the solid was extracted with 10 mL of CH_2Cl_2 and MeOH (v : v = 1 : 1) and filtered again. 20 mL of Et_2O was layered on the filtrate to afford blue plates of **1**·3CH_2Cl_2, which were isolated by filtration, washed with MeOH and dried in air. Yield: 221 mg (89% based on Cu). Anal. Calc. for $C_{26}H_{32}Cu_4N_4O_{20}$: C, 30.04; H, 3.31; N, 5.75%. Found: C, 30.46; H, 3.49; N, 5.36%. IR (KBr disk): 1710 (s), 1687 (m), 1622 (s), 1580 (s), 1508 (w), 1487 (m), 1441 (s), 1347 (m), 1265 (s), 1224 (m), 1181 (w), 1069 (m), 826 (w), 772 (m), 682 (w), 623 (w), 490 (w) cm^{-1}.

$[\{Cu_2(\mu\text{-dcmpz})_2\}(\mu\text{-OMe})_2]_3$ (2)

To a MeOH (10 mL) solution of $Cu(OAc)_2{\cdot}H_2O$ (198 mg, 1.0 mmol) was added a MeOH solution of Hdcmpz (366 mg, 2.0 mmol). The resulting solution was refluxed for 6 h to form a larger amount of blue precipitate. A similar work-up to that used in the isolation of **1** generated blue crystals of **2**. Yield: 235 mg (85% based on Cu). Anal. Calc. for $C_{48}H_{60}Cu_6N_{12}O_{30}$: C, 34.60; H, 3.63; N, 10.09%. Found C, 34.86; H, 3.46; N, 9.79%. IR (KBr disk): 1711 (s), 1687 (m), 1630 (w), 1583 (w), 1512 (w), 1469 (w), 1435 (m), 1407 (w), 1352 (w), 1261 (s), 1123 (w), 1171 (w), 1071 (s), 959 (w), 820 (m), 768 (s), 632 (w), 482 (w), 432 (w) cm^{-1}.

$[\{Cu(MeOH)\}_4(\mu\text{-mcccpz})_4]{\cdot}4MeOH$ (3·4MeOH·0.5H_2O)

To a Pyrex glass tube (15 cm in length, 7 mm in inner diameter) was added $Cu(OAc)_2{\cdot}H_2O$ (101 mg, 0.5 mmol), dcmpz (188 mg, 1.0 mmol) and MeOH (2 mL). The tube was sealed and heated in an oven at 120 °C for one day to form blue solution. The filtrate was kept at −18 °C for several days to form crystalline solids of 3·4MeOH·0.5H_2O, which were isolated by filtration, washed with MeOH and dried in air. Yield: 40 mg (30% based on Cu). Anal. Calc. for $C_{28}H_{28}Cu_4N_8O_{20}$: C, 32.01; H, 2.69; N, 10.66. Found C, 32.47; H, 2.46; N, 10.35%. IR (KBr disk): 1694 (s), 1628 (s), 1516 (m), 1489 (w), 1435 (w), 1392 (w), 1339 (m), 1318 (w), 1286 (m), 1286 (m), 1228 (m), 1070 (s), 1022 (w), 950 (w), 842 (w), 773 (m), 625 (w), 513 (w) cm^{-1}.

Typical procedure for the synthesis of 2-oxazolines

The procedures for the catalytic reactions are the same (Table 5). And a typical reaction is given below (Table 5, entry 1). Benzonitrile (104 mg, 1 mmol), amino alcohol (245 mg, 4 mmol), and **1** (19 mg, 2 mol%) were mixed and stirred for 6 h at 100 °C. After completion of the reaction, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), and filtered. The filtrate was concentrated *in vacuo*, and the resulting residue was purified by silica gel chromatography to provide the desired product.

2-Phenyl-4,5-dihydrooxazole. Colorless oil; ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 7.869–7.845 (d, 2H, J = 7.2 Hz, aromatic CH), 7.394–7.194 (m, 3H, aromatic CH), 4.342–4.279 (t, 2H, CH_2), 3.978–3.915 (t, 2H, CH_2). MS (ESI): m/z = 148.1 $[M + 1]^+$.

2-(*p*-Tolyl)-4,5-dihydrooxazole. White solid; mp: 67–68 °C (lit.[11a] mp 71–73 °C). ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 7.847–7.820 (d, 2H, J = 8.1 Hz, aromatic CH), 7.222–7.196 (d, 2H, J = 7.8 Hz, aromatic CH), 4.442–4.379 (t, 2H, CH_2), 4.072–4.009 (t, 2H, CH_2), 2.384 (s, 3H, CH_3). MS (EI): m/z = 162.1 $[M + 1]^+$.

2-(*m*-Tolyl)-4,5-dihydrooxazole. Colorless oil; ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 7.719 (s, 1H, aromatic CH), 7.696–7.663 (m, 1H, aromatic CH), 7.234–7.217 (m, 2H, aromatic CH), 4.380–4.317 (t, 2H, CH_2), 4.008–3.945 (t, 2H, CH_2), 2.315 (s, 3H, CH_3). MS (EI): m/z = 162.1 $[M + 1]^+$.

2-(*o*-Tolyl)-4,5-dihydrooxazole. Colorless oil; ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 7.884–7.829 (m, 1H, aromatic CH), 7.610–7.585 (d, 1H, aromatic CH), 7.493–7.452 (m, 1H, aromatic CH), 7.389–7.242 (m, 1H, aromatic CH), 4.502–4.439 (t, 2H, CH_2), 4.162–4.099 (t, 2H, CH_2), 2.552 (s, 3H, CH_3). MS (EI): m/z = 162.1 $[M + 1]^+$.

2-(4-Nitrophenyl)-4,5-dihydrooxazole. Slightly yellow solid; mp: 175–177 °C (lit.[11a] mp 180–181 °C). ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 8.279–8.251 (d, 2H, J = 8.4 Hz, aromatic CH),

Table 5 Crystal data and the structure refinement parameters for **1**·3CH_2Cl_2, **2**, and **3**·4MeOH·0.5H_2O

Compounds	**1**·3CH_2Cl_2	**2**	**3**·4MeOH·0.5H_2O
Formula	$C_{29}H_{38}Cl_6Cu_4N_4O_{20}$	$C_{48}H_{60}Cu_6N_{12}O_{30}$	$C_{64}H_{90}Cu_8N_{16}O_{49}$
Formula weight	1229.49	1666.32	2375.84
Crystal system	Triclinic	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$I4_1/a$
a/Å	12.3277(5)	15.722(3)	15.5074(10)
b/Å	13.9177(5)	16.304(3)	15.5074(10)
c/Å	14.9095(5)	16.721(3)	19.8920(12)
α (°)	69.705(3)	95.39(3)	
β (°)	72.104(3)	115.01(3)	
γ (°)	87.298(3)	114.83(3)	
V/Å^3	2278.11(15)	3327.6(11)	4783.6(5)
D_c/(g cm^{-3})	1.792	1.663	1.626
Z	2	2	2
μ (Mo Kα)/mm^{-1}	2.271	1.976	1.845
F(000)	1236	1692	2352
Total reflections	20 777	184 702	35 860
Unique reflections	8452	22 193	3106
No observations	6800	18 161	2337
No parameters	576	883	157
R_{int}	0.0355	0.0325	0.0516
R^a	0.0439	0.0312	0.0590
wR^b	0.1065	0.0772	0.1780
GOF^c	1.052	1.040	1.068

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} w$R = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. ^{c} GOF = $\{\sum w((F_o^2 - F_c^2)^2)/(n - p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

8.129–8.101 (d, 2H, J = 8.4 Hz, aromatic CH), 4.536–4.472 (t, 2H, CH_2), 4.156–4.093 (t, 2H, CH_2). MS (EI): m/z = 193.1 $[M + 1]^+$.

2-(Pyridin-4-yl)-4,5-dihydrooxazole. White solid; mp: 106–107 °C (lit.[11a] mp 111–112 °C). ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 8.685–8.669 (d, 2H, J = 4.8 Hz, aromatic CH), 7.752–7.733 (d, 2H, J = 5.7 Hz, aromatic CH), 4.469–4.405 (t, 2H, CH_2), 4.095–4.031 (t, 2H, CH_2). MS (EI): m/z = 149.1 $[M + 1]^+$.

2-(Pyridin-3-yl)-4,5-dihydrooxazole. White solid; mp: 65–66 °C (lit.[11a] mp 68–69 °C). ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 9.125 (s, 1H, aromatic CH), 8.682–8.669 (d, 1H, J = 3.9 Hz, aromatic CH), 8.199–8.173 (d, 1H, J = 7.8 Hz, aromatic CH), 7.346–7.304 (m, 1H, aromatic CH), 4.468–4.404 (t, 2H, CH_2), 4.088–4.025 (t, 2H, CH_2). MS (EI): m/z = 149.1 $[M + 1]^+$.

4-(4,5-Dihydrooxazol-2-yl)aniline. Slightly yellow solid. mp: 156–158 °C (lit.[27] mp 160–161 °C. ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 7.752–7.724 (d, 2H, J = 8.4 Hz, aromatic CH), 6.657–6.629 (d, 1H, J = 8.4 Hz, aromatic CH), 4.405–4.342 (t, 2H, CH_2), 4.028–3.966 (t, 2H, CH_2). MS (EI): m/z = 163.1 $[M + 1]^+$.

2-(Naphthalen-2-yl)-4,5-dihydrooxazole. White solid; mp: 83–85 °C (lit.[28] mp 84–85 °C). ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 8.443 (s, 1H, aromatic CH), 8.058–8.029 (d, 1H, J = 8.7 Hz, aromatic CH), 7.918–7.874 (m, 3H, aromatic CH), 7.543–7.483 (m, 2H, aromatic CH), 4.511–4.448 (t, 2H, CH_2), 4.142–4.080 (t, 2H, CH_2). MS (EI): m/z = 198.1 $[M + 1]^+$.

2-(4-(1*H*-Pyrazol-3-yl)phenyl)-4,5-dihydrooxazole. White solid; mp: 167–169 °C. ^{1}H NMR ($CDCl_3$, ppm, 300 Hz): δ 7.988–7.961 (d, J = 8.1 Hz, 2H), 7.826–7.799 (t, J = 8.1 Hz, 2H), 7.614 (s, 1H), 6.661 (s, 1H), 4.482–4.420 (t, 2H), 4.115–4.052 (t, 2H). ^{13}C NMR ($CDCl_3$, ppm, 75 MHz): δ 164.9, 149.4, 135.6, 132.7, 129.0, 127.3, 125.9, 103.5, 68.0, 55.2. HRMS calcd for $C_{12}H_{11}N_3O$ 214.0975, Found 214.0966. Anal. Calcd for $C_{12}H_{11}N_3O$: C, 67.59, H, 5.20, N, 19.71. Found: C, 67.33, H, 4.95, N, 19.54.

X-ray structure determinations

X-ray quality crystals of **1**·3CH_2Cl_2, **2**, and **3**·4MeOH·0.5H_2O were obtained directly from the above preparations. Single crystals of **1**·3CH_2Cl_2, **2**, and **3**·4MeOH·0.5H_2O were mounted on glass fibers with grease and cooled in a liquid nitrogen stream at 200 K (**1**·3CH_2Cl_2 and **2**) or 173 K (**3**·4MeOH·0.5H_2O). Crystallographic measurements were made on a Xcalibur Atlas Gemini (**1**·3CH_2Cl_2), or Bruker APEX-II CCD (**2** and **3**·4MeOH·0.5H_2O) diffractometer by using graphite-monochromated Mo-Kα (λ = 0.71070 Å). Diffraction data were collected at ω mode with a detector distance of 35 mm to the crystals. The collected data were reduced by using the program *CrysAlisPro, Agilent Technologies* (CrysAlis171. NET, Version 1.171.36.28) or *Bruker APEX2* and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1**·3CH_2Cl_2, **2**, and **3**·4MeOH·0.5H_2O were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the SHELXTL-97 program.[29] In **1**·3CH_2Cl_2, one CH_2Cl_2 molecule was split into two sites with an occupancy ratio of 0.5/0.5 for Cl(2)/Cl(2A) and C(27)/C(27A). In **3**·4MeOH·0.5H_2O, the uncoordinated MeOH molecule was split into two sites with an occupancy ratio of 0.5/0.5 for O(6)/O(6A) and C(8)/C(8A). The H_2O molecule was refined to one-eighth-occupancy to give acceptable thermal parameters. Except for O(6), C(8) atoms of MeOH molecule and O(7) atom of H_2O molecule in **3**·4MeOH·0.5H_2O, all non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. Hydrogen atoms of the disordered MeOH molecule (O(6), C(8) and O(6A), C(8A)) and the uncoordinated water molecule (O(7)) in **3**·4MeOH·0.5H_2O were not located. The hydrogen atom of O(5) from the coordinated MeOH molecule was firstly located from Fourier maps and subsequently the O–H bond was fixed to be 0.86 Å. All other hydrogen atoms introduced at the calculated positions and included in the structure-factor calculations. A summary of the important crystallographic information for **1**·3CH_2Cl_2, **2**, and **3**·4MeOH·0.5H_2O are summarized in Table 5.

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