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Synthesis, characterization and catalytic properties of a new binuclear copper(II) complex in the azide–alkyne cycloaddition

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Abstract

A new binuclear copper(II)-oxalate complex containing 2,9-dimethyl-1,10-phenanthroline (dmp), was synthesized via a simple and one-pot reaction. $[Cu_2(dmp)_2(ox)Cl_2]\cdot H_2O$ (1) was characterized by single-crystal X-ray crystallography and IR methods. The complex 1 was been used to efficiently catalyze the three-component 1,3-Dipolar cycloaddition CuAAC reaction to produce 1,4-disubstituted 1,2,3-triazoles in good to excellent yields from aromatic or aliphatic halide, sodium azide, and acetylene in water as a green solvent with low catalyst amount.

Keywords: CuAAC reaction; 1,2,3-Triazole; Crystal structures; Binuclear Cu(II) complex

Introduction

"Click chemistry" as a powerful route to the simple and high yielding synthesis of irreversible C-C or C-X (X = heteroatom) bonds, is an interesting concept to the preparation of various chemicals and pharmaceutical compounds [1–4]. In fact, this idea was presented by Sharpless and coworkers for the first time and consists on modern organic synthesis among selective, atom economically, various molecules generation, high yield with safe (or no) side-product and easy experimentally routes [5–9]. A combination of click chemistry and green chemistry can provide some rapid, effective and as well as environmentally friendly procedures [10]. 1,3-dipolar azide-

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alkyne cycloaddition reaction is one of the most well-known and powerful click chemistry reactions because of their development in rate and regioselectivity [11,12]. The five-membered heterocyclic 1,2,3-triazoles as synthetically and biologically valuable compounds are the products of these reactions [13].

The application of transition metal complexes in wide range fields such as catalysis, material sciences, nanotechnology and biological sciences makes them as important compounds [14]. In recent decades, di- and poly-nuclear Cu(II) complexes due to their variety in structure, distortion in coordination geometry and application in the catalytic systems, medical sciences, biochemistry and sensing devices have attracted significant interest [15]. Copper-based complexes and materials because of their widespread oxidation states (0, I, II and III) and subsequently their ability to promote reactions via one and two-electron pathways, have many attractions for use as organic transformations catalysts such as copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction [16]. CuAAC catalytic system has some significant advantages such as moderate heating condition, regioselectivity, broad area, green chemistry medium, and tolerate the existence of high functional groups [17–20]. The Cu was applied as an efficient catalyst for the synthesis of 1,2,3-triazoles in both ionic and complex forms (metal or salt) [21,22] and using of this method (CuAAC) is one of the well-known procedures in modern organic synthesis [23,24].

Herein, we report a newly binuclear copper complex synthesis route with 2,9-dimethyl-1,10phenanthroline bidentate ligand and oxalate anion as a bridge between Cu atoms and its characterization with single-crystal X-ray crystallography. The application of this complex as an effective catalyst in the selective formation of various 1,4-disubstituted 1,2,3-triazoles was also investigated.

Experimental Section

Chemicals and materials

The chemicals and solvents were supplied from commercial sources and used without further purification.

Synthesis of [Cu₂(dmp)₂(ox)Cl₂].H₂O (1)

 $[Cu_2(dmp)_2(ox)Cl_2]$ was synthesized as follows: a certain amount of of CuCl_2.2H_2O (68 mg, 0.40 mmol) was dissolved in H₂O (20 mL) and obtained solution was successively added to a mixed solution of 2,9-dimethyl-1,10-phenanthroline (62 mg, 0.40 mmol) in ethanol (10 mL) and oxalic acid (25 mg, 0.20 mmol) in water (10 mL) under stirring. The final solution was heated to 80 °C for 1 h and then filtered. After some days standing and slowly evaporating, green crystals were obtained at room temperature and a suitable single crystal of them chosen to X-ray diffraction study.

Synthesis of alkyl azides

Alkyl azides was prepared according to reported procedure with some modification [25]. Sodium azide (360 mg, 5.5 mmol) was added to 11 mL DMSO and stirred for 24 h at room temperature. Then, the alkyl bromide (5.0 mmol) was transferred to the previous solution and the mixture was stirred for 4 h. Diethyl ether (2 ×20 mL) was used to extraction of the obtained product. The extracted solution was washed with water (2 ×20 mL) and then dried with MgSO₄ and the solvent was removed under reduced pressure to obtain pure alkyl azide.

Typical experimental procedure for the click reaction

A mixture of the alkyne (0.5 mmol), benzyl halide (0.52 mmol) and sodium azide (0.55 mmol) was successively added to $[Cu_2(dmp)_2(ox)Cl_2]$ (0.004 mmol) in 2 mL water and heated at 70 °C for 6 h (for aliphatic azides, alkyl azide (0.52 mmol) were used instead of benzyl halide and sodium azide). Reaction completion was monitored by TLC. After the extraction of the organic layer with ethyl acetate (2×10 mL), the residue water was removed by CaCl₂. The ethyl acetate was eliminated under vacuum to obtain the corresponding product. The recovered catalyst washed with ether and ethyl acetate, dried and then utilized for the next run.

Results and Discussion

The complex 1 has been successfully synthesized by a one-pot reaction between copper chloride, 2,9-dimethyl-1,10-phenanthroline and oxalic acid. The oxalate bidentate ligand as a bridging group has an imperative position in the binuclear Cu complexes. Heretofore several binuclear copper complexes using oxalate ligand such as $[Cu_2(ox)(phen)_2(H_2O)_2](NO_3)_2.2H_2O$ (phen = 1,10-phenanthroline) [26], $[Cu_2(ox)(phen)_2(C_3H_7NO)_2](ClO_4)_2$ (C_3H_7NO = 2,5-dihydroxy-1,4-dithiane) [27], $[Cu_2(dpq)_2(H_2O)_2(ox)](ClO_4)_2.2H_2O$ (dpq = dipyridoquinoxaline) [28] and

 $[{Cu(NO_3)(H_2O)(bipy)}_2(ox)]$ (bipy = 2,2'-bipyridine) [29] were reported. Also, oxalate ligand binuclear other metal for synthesis of some complexes was used e.g. $[\{(N)_4\}_2M_2(ox)](ClO_4)_2.xH_2O$ (M = Mn, Fe^{II}, Co^{II}; (N)₄ = bispicen, bispicMe₂en; bispicen = N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine, bispictn = N,N'-bis(2-pyridylmethyl)bispicMe₂en = N,N'-bis(2-pyridylmethyl)-N,N'-dimethyl-1,2-1,3-propanediamine, ethanediamine) [30] and $[(acac)_{2}Fe(ox)Fe(acac)_{2}]$ (acac = acetylacetonate) [31]. The structure of [Cu₂(dmp)₂(ox)Cl₂] was determined by the single-crystal X-ray analysis. Crystallographic data and details of the refinement parameters for complex 1 are summarized in Table 1. This compound crystallized in P-1 space group and belongs to the triclinic crystal system. As shown in Fig. 1 and 2, the copper complex 1 is built up of neutral dinuclear [(dmp)ClCu(C₂O₄)CuCl(dmp)] building blocks with an inversion center in the midst of the carbon-carbon bond of the oxalate bridging ligand. The Cu centers linked together by carboxylate bridging ligands and also the complex entities held together by hydrogen bond and π - π interactions. A five-coordinated distorted square pyramidal geometry is observed for each copper center [15,26]. Also, each of copper atoms linked to one 2,9-dimethyl-1,10phenanthroline and one Cl⁻ ligand.



Fig. 1. ORTEP drawing of [Cu₂(dmp)₂(ox)Cl₂]



Fig. 2. Three-dimensional view of network in 1. Yellow: Cu, red: O, blue: N, green: Cl, white: C and white sphere: H

	$[Cu_2(dmp)_2(ox)Cl_2] \bullet H_2O$
Formola	$C_{30}H_{26}Cl_2Cu_2N_4O_5$
Formula weight	720.53
Temperature [K]	173(2)
λ [Å]	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
a [Å]	12.9002(9)
b [Å]	14.9391(10)
c [Å]	31.021(2)
α [°]	103.9179(18)
β [°]	95.984(2)
γ [°]	90.0493(19)
V [Å ³]	5769.1(7)
Z, ρ_{calc} [g cm ⁻³]	2, 2.462

Table 1. Summary of the crystal data and structure refinements for [Cu₂(dmp)₂(ox)Cl₂]

μ [mm ⁻¹]	2.445	
F(000)	2928	
rflns: total	5779	
Abs. corr.	Multi-Scan	
Min., max.	0.7720,0.6110	
Transmission factors		
R1 $[I > 2\sigma(I)]$	0.0461	
wR ₂ (all data)	0.1135	

Fig. 3. shows the average of bond lengths and also the range of bond distances (except C-H bonds) in the compound **1**. The Cu-N bond distances are in the range of 2.001(4)-2.207(4) Å (with a mean length of 2.107 Å). Cu-Cl bond lengths are 2.2390(13) and 2.2706(13) Å. The bond lengths of Cu-O(ox) vary from 1.969(3) to 2.028(3) Å (with an average bond length of 2.004 Å). The average of C(dmp)-N(dmp), C(ox)-O(ox), C(ox)-C(ox), C(dmp)-C(dmp) and C(dmp)-C(Me) bond distances are 1.346, 1.256, 1.521, 1.395 and 1.487 Å, respectively, that are comparable with same bond lengths in the previously reported compounds [32-34]. Also, the N(dmp)-Cu-N(dmp) bond angles (79.49(15) and 79.61(15) °) are smaller than O(ox)-Cu-O(ox) bond angles (82.58(12) and 83.36(12) °).



Fig 3. The average of bond lengths in the compound 1

Catalytic Studies

The catalytic properties of the $[Cu_2(dmp)_2(ox)Cl_2]$ complex were investigated in the synthesis of 1,2,3-triazoles from alkynes, halides and sodium azide as precursors. The reactions were conducted on a model multicomponent procedure of benzyl chloride, phenylacetylene and NaN_3 to studying of azide-alkyne cycloaddition reaction in the present of water as the green solvent under air at 70 °C for 6 h. The reaction conditions were optimized with respect to the solvent, quantity of catalyst, reaction time and the reaction mixture temperature and the results are collected in Table 2. It was found that $[Cu_2(dmp)_2(ox)Cl_2]$ complex showed higher efficiency than catalyst-free condition and CuCl₂ powder (entries 1, 2) in the synthesis of 1-Benzyl-4phenyl-1H-1,2,3-triazole. Solvents have an overriding influence on the azide-alkyne cycloaddition reaction. As can be seen from Table 2, in the comparison of aprotic solvents (acetonitrile, n-hexane, tetrahydrofuran, ethyl acetate and toluene) with protic solvents (water, ethanol and methanol), protic solvents displayed higher performance (entries 3-10). Among all solvents, synthesis of 1-benzyl-4-phenyl-1H-1,2,3-triazole in the presence of water as a green solvent obtained the best isolated yield (99%). For the investigation of the amount of catalyst effect, a series of experiments were carried out by using of 0.001, 0.002, 0.004 and 0.006 mmol Cu₂(dmp)₂(ox)Cl₂ in H₂O at 70 °C for 6 h (entries 10-13), results were illustrated that with increasing of catalyst from 0.001 to 0.004 mmol, an increase in the reaction yield from 73% to 99% was observed. However, further increase in the catalyst amount to 0.006 mmol, didn't have an influence in the isolated yield of triazole product. Based on some results related to the investigation of the influence of temperature in the azide-alkyne cycloaddition reaction, it was observed that increasing reaction mixture temperature has a positive effect on the product yield. Increasing reaction temperature from room temperature to 70 °C leads to increasing reaction yield from 14% to 99% (entries 10 and 14-16). Furthermore, with a view to finding optimal reaction time, we examined the model reaction in different reaction times from 2-8 hours. The maximum yield was achieved when the reaction carried out for 6 h. Above 6 h of the reaction time, no noteworthy change in the reaction yield took place (entries 17-19).

\bigcirc	Cl +		$\frac{1}{N_{\text{Cl}}} \frac{1}{N_{\text{Cl}}} \frac{1}{N_{Cl$		N=N N	
Entry	Catalyst	Solvent	Catalyst dosage (mmol)	Temperature (°C)	Time (h)	Yield ^b (%)
1	-	H_2O	-	70	6	
2	CuCl ₂	H_2O	0.004	70	6	62
3	$Cu_2(dmp)_2(ox)Cl_2$	MeCN	0.004	70	6	56
4	$Cu_2(dmp)_2(ox)Cl_2$	n-hexane	0.004	70	6	2
5	$Cu_2(dmp)_2(ox)Cl_2$	THF	0.004	70	6	10
6	$Cu_2(dmp)_2(ox)Cl_2$	MeCOOEt	0.004	70	6	4
7	$Cu_2(dmp)_2(ox)Cl_2$	Toluene	0.004	70	6	4
8	$Cu_2(dmp)_2(ox)Cl_2$	EtOH	0.004	70	6	82
9	$Cu_2(dmp)_2(ox)Cl_2$	MeOH	0.004	70	6	92
10	$Cu_2(dmp)_2(ox)Cl_2$	H_2O	0.004	70	6	99
11	$Cu_2(dmp)_2(ox)Cl_2$	H_2O	0.001	70	6	73
12	$Cu_2(dmp)_2(ox)Cl_2$	H_2O	0.002	70	6	81
13	$Cu_2(dmp)_2(ox)Cl_2$	H_2O	0.006	70	6	99
14	$Cu_2(dmp)_2(ox)Cl_2$	H_2O	0.004	25	6	14
15	$Cu_2(dmp)_2(ox)Cl_2$	H ₂ O	0.004	40	6	53
16	$Cu_2(dmp)_2(ox)Cl_2$	H ₂ O	0.004	55	6	81
17	$Cu_2(dmp)_2(ox)Cl_2$	H ₂ O	0.004	70	2	75
18	$Cu_2(dmp)_2(ox)Cl_2$	H_2O	0.004	70	4	83
19	$Cu_2(dmp)_2(ox)Cl_2$	H_2O	0.004	70	8	98

Table 2.	The influe	nce of vario	us conditions	on the azide	e–alkvne c	veloaddition
						J • 10 • • • • • • • • • • • •

^a Reaction conditions: phenylacetylene (0.50 mmol), benzyl chloride (0.52 mmol), sodium azide (0.55 mmol), solvent (2.0 mL).

^b Isolated yield.

With this optimal system in hand, various alkynes including phenyl acetylene, propargyl alcohol and dimethyl propargyl alcohol, benzyl halides such as benzyl chloride, 2-methylbenzyl chloride, 4-nitrobenzyl chloride and benzyl bromide, and alkyl halides including azidocyclohexane and 1-azidooctane were examined to the synthesis of triazoles at 70 °C and the results are shown in Table 3. We explored the effect of different substitution on the benzyl chloride (both electron-donating and electron-withdrawing substituted groups) witch reacted with phenylacetylene, results indicated a reduction in the isolated yields for 2-methyl and 4-nitro substituted benzyl chloride versus unsubstituted benzyl chloride (entries 1-3). It seems 2-methyl substituted benzyl chloride due to the steric hindrance effect, showed more decrease in the yield of reaction with phenylacetylene. Substituting the phenylacetylene with propargyl alcohol and dimethyl

propargyl alcohol leads to a decreasing in the reaction yield (entries 4 and 5). Moreover, the reaction of propargyl alcohol and dimethyl propargyl alcohol with benzyl bromide were obtained noticeably higher yields than benzyl chloride (entries 7 and 8).



Table 3. Click reaction of various benzyl halides with terminal alkynes in the presence of 1^a

^a Reaction conditions: alkyne (0.50 mmol), benzyl halide (0.52 mmol), sodium azide (0.55 mmol), catalyst (0.004 mmol), in H₂O (2.0 mL), 70 °C. ^b Isolated yield.

Aliphatic azides were also effectively clicked with the terminal alkynes in the presence of $Cu_2(dmp)_2(ox)Cl_2$ in H₂O at 70 °C for 6 h and yielded relating 1,2,3-triazole products between 62-95% (Table 4). It looks when azidocyclohexane was used, the corresponding product due to the steric hindrance, was obtained in lower yield than in the case of 1-azidooctane (entries 1-4).



Table 4. Cycloaddition of aliphatic azides and terminal alkynes in the presence of catalyst 1^a

Reusability

Reusability of the catalyst is one of the most important features in catalytic reactions. Thus, after the first 1,3-dipolar azide-alkyne cycloaddition reaction, the catalyst was taken out from the reaction mixture by centrifuging and after several times washing with ethyl acetate and diethyl ether, dried at 50 °C overnight and subjected to the second cycle without any additional treatment. Although slow weakening of activity was detected, after three cycles the reaction yield is decreased to 60% (Fig. 4)

^a Reaction conditions: alkyne (0.50 mmol) and alkyl azide (0.52 mmol), catalyst (0.004 mmol), in H₂O (2.0 mL), 70 °C. ^b Isolated yield.



Fig. 4. Recycling studies of the [Cu₂(dmp)₂(ox)Cl₂] in the azide–alkyne cycloaddition reaction

The infrared spectrum of complex 1 before and after of reuse as a catalyst in the wavenumber region 400 to 4000 cm⁻¹ is shown in Fig. 5. The broad and strong peak of hydroxyl group stretching vibration appeared at 3280 cm⁻¹. The band at 1368 cm⁻¹ attributed to C-O symmetry vibration [29]. Peaks with wavenumber from 1426 to 1602 cm⁻¹ are assigned to the C-C and C-N stretching vibration of the phenanthroline rings [35]. The IR spectra of the fresh and reused catalyst are slightly different and a comparison between these two spectra illustrated the decrease in catalytic performance after three cycles are due to destruction and structural changing of the complex 1 under reaction condition.



Fig. 5. Infrared spectra of a) fresh and b) reused complex 1

In order to investigate the catalytic advantages for complex 1, we compared our reported catalyst with some copper-containing complexes in the synthesis of 1,4-disubstituted 1,2,3-triazole from phenylacetylene, benzyl chloride and sodium azide. Under the conditions described in Table 4, the complex 1 in some items is superior to other catalysts. For example, among all of these catalysts, only the compound 1 can complete the azide-alkyne cycloaddition reaction and this is while the lowest amount of catalyst mol% was used in our catalytic system. Furthermore, it was obtained that the complex 1 demonstrated some other preponderances in comparison to other systems, such as using green solvent (entry 5) and low reaction time (entries 2, 3 and 5).

Entry	Catalyst	Conditions	Yield (%)	Ref.
1	$[Cu_2(dmp)_2(ox)Cl_2] \cdot H_2O$	Catalyst: 0.8 mol%/2 mL $H_2O/6$ h/70	99	present
		°C		work
2	$[CuL_2], HL = 1-$	Catalyst: 1.4 mol%/2 mL H ₂ O/12	95	[36]
	((4-bromophenylimino)methyl)na	h/70 °C		

Table 5. Azide-alkyne cycloaddition reaction with various Cu-containing complexes

	phthalen-2-ol			
3	$[Cu(tzol)_2], tzol = 2-$	Catalyst: 2 mol%/ 2 mL H ₂ O/12 h/70	96	[37]
	(2'-hydroxyphenyl)-2-thiazoline	°C		
4	[(NHC)CuI], NHC = 5,6-	Catalyst: 3 mol%/1 mL $H_2O/2$ h/r.t.	32	[38]
	Dimethyl-1,3-bis(2,3,4,5,6-pentam			
	ethylbenzyl)-2,3-dihydro-1H-benz			
	o[d]imidazol-2-yl			
5	$TBA_4H_2[\gamma-$	Catalyst: 2 mol%/2 mL	81	[39]
	$SiW_{10}O_{36}Cu_2(\mu-1,1-N_3)_2], TBA =$	CH ₃ CN/CH ₃ OH/31 h/60 °C		
	tetrabutylammonium			

Conclusion

In summary, a binuclear Cu(II) complex was synthesized by reaction of copper(II) chloride with 2,9-dimethyl-1,10-phenanthroline ligand and oxalic acid. This complex has been used as a catalyst in the 1,3-dipolar cycloaddition reaction of benzyl chloride, phenylacetylene and NaN₃ for the generation of 1,2,3-triazoles. The catalyst **1** exhibited high catalytic activity for cycloaddition reaction of different organic halides and terminal acetylenes in water. Additionally, this compound is a reusable catalyst at least for three runs.

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Supplementary Data

The CIF file of crystal structure complex, [Cu₂(dmp)₂(ox)Cl₂]·H₂O has been deposited with the CCDC, No. 1991276. This free of data can be obtained charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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Graphical abstract-S

The azide–alkyne cycloaddition reactions were conducted by a new binuclear copper(II)–oxalate complex containing 2,9-dimethyl-1,10-phenanthroline without any additional agents.

Highlights

- 1. A new binuclear copper(II)-oxalate complex containing 2,9-dimethyl-1,10-phenanthroline is synthesized.
- 2. The complex is applied for the three-component 1,3-Dipolar cycloaddition CuAAC reaction .
- 3. Excellent yield has been achieved.