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Copper (I) complex of 2,9-dimethyl-1,10-phenanthroline: synthesis, structure, and catalytic properties

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Dedicated to Professor Mojtaba Bagherzadeh, my dear supervisor at Sharif University of Technology, for the helpful guidances, encouragement and valuable comments he has been providing me to improve my scientific level and life issues.

Abstract

A copper (I) complex containing 2,9-dimethyl-1,10-phenanthroline (dmph), [Cu(dmph)₂]Cl·6H₂O, was prepared by reaction of CuCl₂·2H₂O and 2,9-dimethyl-1,10phenanthroline in an aqueous solution at pH=11 and characterized using elemental analysis, IR, EDX and X-ray crystallography. The complex consists of a mononuclear copper (I) surrounded by four coordinating nitrogen atoms of two dmph ligands, one Cl⁻ anion and six H₂O molecules. This novel cupper (I) complex was used as a catalyst for alkyne–azide cycloaddition (CuAAC) reaction to produce several 1,2,3-triazoles in high yields. The presented catalytic system fulfils the requirements of "click chemistry" with its soft and appropriate conditions, notably in water as solvent with low catalyst amount without any co-catalyst or activator.

Keywords: Complex; Copper; Phenanthroline; Azide- alkyne cycloaddition

Introduction

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Phenanthroline complexes of transition metal have been widely studied by researchers because of their diverse applications in electrochemistry, photochemistry, materials science and bioinorganic chemistry [1–8]. In particular, Cu-complexes containing phenanthroline ligands have applications in the field of inorganic photochemistry, modeling enzyme activity, solar energy conversion, and cleavage of DNA [9-15].

1,3-Dipolar cycloaddition reaction is powerful strategy for the synthesis of various functional 1,2,3-triazole molecules from organic azides and terminal alkynes as simple starting materials [16-21]. Among various metal catalysts for cycloaddition process, copper (I)- catalyzed 1,3-dipolar cycloaddition reaction proved to be the most versatile for the synthesis of 1,2,3-triazoles in recent years [22-25].

We herein report synthesis and characterization of a copper (I) complex of 2,9-dimethyl-1,10phenanthroline (dmph) with using a copper (II) source by one-step method (Scheme 1). Further we study the catalytic activity of this complex $[Cu(dmph)_2]Cl\cdot 6H_2O$, for the 1,3-dipolar cycloaddition reaction of terminal alkynes and in situ generated azides to synthesize 1,2,3triazoles under ambient conditions.



Scheme 1. Synthesis of complex [Cu(dmph)₂]Cl

Experimental

Materials and Methods

All chemicals were received from commercial reagent suppliers and used without purification. Copper chloride dehydrate and 2,9-dimethyl-1,10-phenanthroline were purchased from Sigma-Aldrich. Complex [Cu(dmph)₂]Cl₂ was synthesized according to a published procedure [26]. The

composition of the obtained crystals was checked with energy dispersive spectrometry (EDS) as well as with a Perkin-Elmer 240 elemental analyser. EDS spectra were acquired and analysed using an EDAX Pegasus XM4 spectrometer with SDD Apollo 4D detector mounted on a FEI Nova NanoSEM 230 microscope.

Synthesis of complex [Cu(dmph)₂]Cl·6H₂O

A solution of CuCl₂·2H₂O (0.17g, 1.00 mmol) and Na₂CO₃ (1 M, 1.0 mL) in 5.0 mL of H₂O was added to a mixture solution of methanol and water (1:1 V/V, 20 mL) of 2,9-dimethyl-1,10-phenanthroline (0.21 g, 1.00 mmol) and sodium terephthalate (0.166 g, 1.00 mmol). The mixture solution was adjusted with NH₃·H₂O to pH = 11 and allowed to stand at room temperature. Orange-red needle crystals were grown by slow evaporation for over 2-3 days. Yield: 37%. IR (KBr, 500–4000 cm⁻¹): 3040, 2918. 1635, 1508, 1363, 855, 730, 547. Anal. Calcd for C₂₈H₃₆ClCuN₄O₆: C, 53.93; H, 5.82; Cl, 5.68; Cu, 10.19; N, 8.98 and O, 15.39%. Found: C, 54.04; H, 5.92; Cl, 5.71 and N, 9.08 %.

General procedure for the azide-alkyne cycloaddition

Alkyne (0.5mmol), the organic halide (0.55mmol) and NaN₃ (0.55mmol) were added to a solution of $[Cu(dmph)_2]Cl\cdot 6H_2O$ in 2 mL of H₂O. The reaction mixture was warmed to 70 °C and stirred and monitored by TLC. After a certain time, the resulting mixture was extracted with EtOAc (2× 10 mL). The collected organic phase was dried with anhydrous CaCl₂ and the solvent was removed to give the corresponding triazoles, with no purification step.

Single crystal X-ray data collection.

X-ray intensity data for the $[Cu(dmph)_2]Cl\cdot 6H_2O$ crystal were collected using graphite monochromatic Mo K α radiation on a four-circle κ geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector. The ω -scan technique with $\Delta \omega = 1.0^{\circ}$ for each image was used for data collection. One image was used as a standard after every 40 images for monitoring of the crystal stability and data collection, and no correction on the relative intensity variations was necessary. Data collections were made using the CrysAlis CCD program [27]. Integration, scaling of the reflections, correction for Lorenz and polarisation effects and absorption

corrections were performed using the CrysAlis Red program [27]. The structure was solved by the direct methods using SHELXS97 [28] and refined using SHELXL-2014 program [29]. The hydrogen atoms were placed in their geometrical positions. The hydrogen atoms of one disordered water molecule were not localised. The occupation factors of disordered water molecule were refined and they are ~0.68 and ~0.32 for O6 and O7, respectively. The final difference Fourier maps showed no peaks of chemical significance. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Selected geometrical parameters are listed in Table 2 and the geometry of hydrogen bonding interactions are collected in Table 3. Visualisation of the structure was made with the Diamond 3.0 program [30].

Results and Discussion

The composition of the prepared copper (I) complex, $[Cu(dmph)_2]Cl\cdot 6H_2O$, was characterized by the elemental analyses, energy-dispersive X-ray spectroscopy (EDX) and IR, which confirmed the successful assignment of composition for the complex. According to the EDX analysis, the copper/chloride ratio of ~1 and it is in agreement to the atomic ratio in the formula $[Cu(dmph)_2]Cl\cdot 6H_2O$.

The complex is stable enough to handle in air and can be stored for some days. The complex $[Cu(dmph)_2]Cl\cdot 6H_2O$ is not soluble in hexane and toluene, but is highly soluble in ethanol, methanol and acetonitrile and slightly soluble in water. The view of the molecular structure of $[Cu(dmph)_2]Cl\cdot 6H_2O$ complex is shown in Figure 1. The environment of the metal center exhibits a distorted tetrahedral geometry. The asymmetric unit of $[Cu(dmph)_2]Cl\cdot 6H_2O$ consists of one copper (I) cation which is surrounded by four coordinating nitrogen atoms of the two 2,9-methyl-1,10-phenanthroline ligands, one Cl^- anion and six H₂O molecules. However, one of the water molecules is disordered and occupied two positions (see Fig. 1) The Cu—N bonds linking the phenanthroline ligands are in the range of 2.038(3)–2.062(3) Å, and are comparable with those observed for $[Cu(dpp)_2](PF_6)$, $[Cu(tmp)_2]BPh_4$ and $[Cu(dpdmp)_2]PF_6$ [31, 32]. Angular distortions from the perfect tetrahedral geometry result from the chelating ligands. A search of the CCDC Data Base (Version 5.39, November 2017) for structures containing the [Cu(dmph)_2]⁺

cation yields over 40 structures, in which quite similar distorted tetrahedral environment of Cu(I) cation as present in the investigated $[Cu(dmph)_2]Cl\cdot 6H_2O$ compound is observed [33]. Most of them contain various organic and inorganic anions to compensate the charge of the cation as well as the different solvent molecules. One of them is the bromide analogue of the our $[Cu(dmph)_2]Cl$ complex, however the bromide analogue crystallizes as monohydrate in the centrosymmetric space group P2₁/c of monoclinic system [34], but our crystallizes in the triclinic system as hexahydrate. Different composition of Br and Cl analogues (Br-monohydrate and Cl-hexahydrate) results in different arrangement and the crystal packing.



Fig. 1 View of the complex [Cu(dmph)₂]Cl·6H₂O with labelling of the atoms. Thermal ellipsoids are drawn at the 50% probability level, H atoms with arbitrary radii.

Empirical formula	$C_{28}H_{36}ClCuN_4O_6$
Formula weight (g·mol ⁻¹)	623.59
Crystal system, space group	Triclinic, P-1
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0714(3), 15.1500(8), 15.2370(9)
α, β, γ (°)	110.60(1), 101.03(2), 93.37(1)
$V(\text{\AA}^3)$	1485.57(19)
Ζ	2
$D_{\rm calc}~({ m g\cdot cm^{-3}})$	1.390
$\mu (mm^{-1})$	0.883
F(000)	648
Crystal size (mm)	0.26 x 0.11 x 0.10
Radiation type, wavelength, λ (Å)	Μο Κα , 0.71073
Temperature (K)	100(1)
θ range(°)	2.414 ÷ 29.624
Absorption correction	multi-scan
T_{\min}/T_{\max}	0.921 / 1.000
Reflections collected / unique / observed	26534 / 7341 / 4378
R _{int}	0.0578
L.S. parameters	375
Refinement on	F^2
$R[F^2>2\sigma(F^2)]$	0.0725
$wR(F^2$ all reflections) ^a	0.1561
Goodness-of-fit, S	1.008
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} \ (e \ {\rm \AA}^{-3})$	+1.041, -0.798

Table 1. Crystal data and structure refinement parameters	lor		(amp	1) ₂	U	·0H	120	J
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^{*a*}) $wR = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{\frac{1}{2}}; w^{-1} = [\sigma^2(F_o^2) + (0.0622P)^2], \text{ where } P = (F_o^2 + 2F_c^2) / 3. \}$

engths (Å)	Bond angles (°)		
2.062(3)	N1-Cu-N2	82.5(1)	
2.049(3)	N1-Cu-N3	132.5(1)	
2.038(3)	N1-Cu-N4	117.5(1)	
2.056(3)	N2-Cu-N2	118.5(1)	
1.312(4)	N2-Cu-N2	131.4(1)	
1.357(5)	N3-Cu-N4	81.7(1)	
	engths (Å) 2.062(3) 2.049(3) 2.038(3) 2.056(3) 1.312(4) 1.357(5)	engths (Å)Bond an,2.062(3)N1-Cu-N22.049(3)N1-Cu-N32.038(3)N1-Cu-N42.056(3)N2-Cu-N21.312(4)N2-Cu-N21.357(5)N3-Cu-N4	

Table 2. Selected bond lengths [Å] and angles $[\circ]$ for $[Cu(dmph)_2]Cl \cdot 6H_2O$

The crystal packing structure of complex $[Cu(dmph)_2]Cl·6H_2O$ is shown in Figure 2. The cationic $[Cu(dmph)_2]^+$ units related by an inversion and translation along a-axis form stacks along the [100] direction (Fig. 2b). The average planes of the 2,9-methyl-1,10-phenanthroline ligand of neighboring cationic $[Cu(dmph)_2]^+$ units related by an inversion are separated by ~3.37(2) Å. This value is comparable with a distance of 3.4 Å for the interacting aromatic rings. The O—H^{...}O hydrogen bonded water molecules together with the O—H^{...}Cl interactions (Table 3) are arranged into pseudo-one-dimensional anionic chains aligned along the *a*-axis (Fig. 2). Both oppositely charged units, i.e. the stacks of π - π interacted $[Cu(dmph)_2]^+$ units and the pseudo-one-dimensional anionic chains, interact each other and stabilize the architecture of the crystal. The arrangement of water rich $[Cu(dmph)_2]Cl·6H_2O$ molecules is different to that of the bromide analogue monohydrate, especially in arrangement of the hydrogen bonded water molecules that together with the chloride anions form tapes along *a*-axis, whereas in the bromide analogue monohydrate the water molecule acts as donor in O-H^{...}Br hydrogen bond forming ^{...}H-O-H^{...}Br^{...}Zigzag chains along *c*-axis [34].

D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A
01—H1 <i>0</i> 1…05	0.82	2.43	3.064 (4)	135.6
$O1$ — $H2O1$ ··· $C11^{i}$	0.83	2.11	2.916 (4)	165.4
O2—H1 <i>O</i> 2⋯O1	0.83	2.00	2.755 (5)	150.6
O2— $H2O2$ ···Cl1 ^{<i>ii</i>}	0.80	2.32	3.102 (4)	163.5
O3—H1 <i>O</i> 3…O4	0.82	2.14	2.818 (6)	140.0
O3—H2O3…O1	0.82	2.04	2.814 (4)	157.4
O4— $H1O4$ ···· $C11$ ⁱⁱⁱ	0.83	2.60	3.392 (4)	159.4

Table 3. Hydrogen-bond geometry (Å, °)

$O4$ — $H2O4$ ···· $C11^{ii}$	0.87	1.99	2.859 (5)	178.2
O5—H1 <i>O</i> 5…O1	0.90	2.77	3.064 (4)	100.3
$O5-H2O5\cdots O7^{iv}$	0.82	1.64	2.311 (10)	137.7

Symmetry codes: (*i*) -*x*, -*y*+1, -*z*+1; (*ii*) -*x*+1, -*y*+1, -*z*+1; (*iii*) *x*+1, *y*, *z*; (*iv*) *x*-1, *y*, *z*.





Fig 2. The crystal packing structure of the complex $[Cu(dmph)_2]Cl\cdot 6H_2O$ viewed along *a*-axis (a) and *c*-axis (b). The H atoms of 2,9-methyl-1,10-phenanthroline ligands are omitted for clarity. Black dashed lines represent O—H^{...}O hydrogen bonds between the water molecules and the red dashed linens represent the O—H^{...}Cl interactions.

Catalytic effects

The considerable stability of the complex [Cu(dmph)₂]Cl toward heat, oxygen and moisture prompted us to use it as a catalyst in the 1,3-dipolar cycloaddition reaction of in situ generated azides and terminal alkynes in water. To find the optimum condition for the cycloaddition reactions, the catalytic potential of the complex [Cu(dmph)₂]Cl was explored in a cycloaddition reaction of benzyl chloride (0.5 mmol), phenylacetylene (0.55 mmol) and NaN₃ (0.5 mmol) as model reactants to form 1,2,3-triazole (Table 4). In the absence of catalyst, reaction is not occurred between reactants, but with 0.32 mol% catalyst loading, the reaction was carried out at 70 °C and product was isolated in 97% yield after 12 h in water under atmospheric conditions (Table 1, entries 1,2). In order to compare the efficacy of complex $[Cu(dmph)_2]Cl$ with others simple sources of copper such as $CuCl_2 \cdot 2H_2O$ and $[Cu(dmph)_2]Cl_2$ the following reactions were performed. Using the copper catalysts, CuCl₂·2H₂O and [Cu(dmph)₂]Cl₂, under the same conditions, the triazole was obtained with a 63% and 50% yield respectively (entries 3, 4). Satisfyingly, it was found that water is a suitable solvent for cycloaddition reaction and product is isolated in 97% yield, but the reaction gave poor results if other solvents, such as ethanol, toluene, acetonitrile and acetone, were screened as solvents, maybe because of the poor solubility of NaN₃ and catalyst in them (entries 4-8). The azide–alkyne cycloaddition reaction was further conducted under a series of temperatures and we found that the reaction does not occur at room temperature (entry 9), while at high temperatures (e.g. 40-70 °C) a significant increase in the product yield was achieved (entries 10, 11). After 12 hours, 1-benzyl-4-phenyl-1,2,3-traizole was isolated in 97% yield at 70 °C (entry 2) and thus, temperature 70 °C was chosen as the optimum reaction temperature in all of the experiments hereafter. Also, in reaction times of less than 12 hours, low amount of the cycloaddition product was isolated, (entries 12–15).

>~						
	Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield $(\%)^a$
-	1	-	H ₂ O	70	12	0
	2	[Cu(dmph) ₂]Cl	H_2O	70	12	97
	3	$CuCl_2$	H_2O	70	12	63
	4	$[Cu(dmph)_2]Cl_2$	H_2O	70	12	50
	5	[Cu(dmph) ₂]Cl	C ₂ H ₅ OH	70	12	70
	6	[Cu(dmph) ₂]Cl	CH ₃ CN	70	12	30

Table 4. The results for different conditions on the azide-alkyne cycloaddition

7	[Cu(dmph) ₂]Cl	toluene	70	12	5
8	[Cu(dmph) ₂]Cl	acetone	70	12	90
9	[Cu(dmph) ₂]Cl	H_2O	r.t.	12	20
10	[Cu(dmph) ₂]Cl	H_2O	40	12	40
11	[Cu(dmph) ₂]Cl	H_2O	60	12	90
12	[Cu(dmph) ₂]Cl	H_2O	70	2	10
13	[Cu(dmph) ₂]Cl	H_2O	70	4	25
14	[Cu(dmph) ₂]Cl	H_2O	70	8	75
15	[Cu(dmph) ₂]Cl	H ₂ O	70	10	95

^aIsolated yield.

To further evaluate the scope of the complex [Cu(dmph)₂]Cl·6H₂O, the same process was successfully applied to a wide range of diversely substituted phenylacetylenes and a mixture of benzyl halides and NaN₃ under the optimal conditions. As demonstrated in Table 5, a single regioisomer, namely 1,4-disubstituted 1,2,3-triazoles, was obtained in 19-95% yields (entries 1-11). Substrates with electron-donating and electron-withdrawing groups in the aryl ring were all directly converted into desired 1,2,3-triazoles in good yields (entries 2-4), but the reactivity of benzyl chlorides with electron-withdrawing substituent was higher than those with electron-donating substituent (entries 2-4). Due to the steric hindrance of the *ortho* substituents on the benzyl halides, benzyl chloride substituted with nitro group at *ortho* position was less reactive to the cycloaddition reaction than the para derivative (entries 3, 4). Replacement of benzyl bromide with benzyl chloride showed a conclusive effect on the isolated yield of 1,2,3-triazoles products (entries 8-11). However, the cycloadditions of aliphatic alkyne containing -OH group, propargyl alcohol, 3-butyn-2-ol and 2-methyl-3-butyn-2-olproceed with lower yield (entries 5-7, 9-11).

Table 5. Cycloaddition of various substrates in the presence of the complex [Cu(dmph)₂]Cl·6H₂O

Entry	Benzyl halide	Alkyne	Yield (%)
1	CI		97
2	CI		60



To check the reusability of the catalyst, after extraction of cycloaddition product, aqueous media containing dissolved $[Cu(dmph)_2]Cl\cdot 6H_2O$ was reused for the next batch of reaction by addition of fresh substrates. The yield of cycloaddition product was found to be decreased by 41 % by the second recycle. This decrease in the yield may be due to degradation of complex during reaction condition, which reduces the catalytic activity of $[Cu(dmph)_2]Cl\cdot 6H_2O$ upon repeated use.

A reaction mechanism proposed for the $[Cu(dmph)_2]Cl \cdot 6H_2O$ catalysed 1,3-dipolar cycloaddition which lead to 1,4-disubstitued 1,2,3-triazoles is outlined in Scheme 2 on the basis of the previous reports [35, 36]. Reaction is started with the generation of the copper (I) acetylide intermediate *via* attraction of cation $[Cu(dmph)_2]^+$ towards the phenylacetylene. Next, with the addition of azide and formation a six-membered copper metallacycle and next step a copper triazole complex, final 1,2,3-triazole product can form and the $[Cu(dmph)_2]Cl$ catalyst is regenerated.



Scheme 2. Proposed mechanism of [Cu(dmph)₂]Cl·6H₂O catalytic cycle for the formation of 1,2,3-triazole.

Conclusion

In conclusion, we have synthesized a copper (I) complex containing 2,9-dimethyl-1,10phenanthroline and demonstrated that this complex is excellent catalyst for the azide–alkyne cycloaddition reactions of terminal alkynes and in situ generated azides to synthesize 1,2,3triazoles under mild and convenient conditions.

Supplementary Data

The CIF file of crystal structure complex, [Cu(dmph)₂]Cl·6H₂O has been deposited with the CCDC, No. 1581109. This obtained free data can be of 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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Highlights

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