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$CuCl_2$ induced reactions of 6-ethynyl- and 6-cyano-5-aryl-2,2′-bipyridines with various N- and O-nucleophiles in comparison with the reactions of relative 1,2,4-triazines

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Abstract

Meanwhile 5-aryl-6-cyano-2,2′-bipyridines are very stable towards various nucleophiles, addition copper(II) chloride to the reactional mixture facilitates nucleophilic addition to the cyano group dramatically. The cyanobipyridines react easily with water, methanol, ethanolamine in the presence of $CuCl_2$ yielding well-crystallized complexes containing carboxylates, carboximidates or carboxamidines as ligands. 5-Cyano-1,2,4-triazines are more active in the reactions due to higher electron-withdrawing properties of this heterocycle. Due to the same reason acetylene moiety of 5-ethynyl-3-pyridyl-1,2,4-triazine adds water quite easily but in the presence of copper chloride as well.

Keywords: Cu^{II} complexes; 2,2′-bipyridines; 1,2,4-triazines

1. Introduction

Increasing reactivity upon coordination to transition metals has wide applications in chemistry [1]. The activation of molecules containing the nitrile group upon their coordination to a metal atom has been exploited in addition reactions of nucleophiles such as water, alcohols and amines yielding amides [2,3] imidates [4] or amidines [5] complexes. The reaction of pyridine-2-carbonitrile was found to be activated by some metal (II) salts yielding complexes of pyridine-2-carboxamide, *O*-alkylpyridine-2-carboximidate or 2-pyridyl-oxazolines-2 [6–8]. Coordination induced nucleophilic substitution of hydrogen at the α-position was observed in reactions of 2,2′-bipyridine and 1,10-phenantroline with water in the presence of transition metals salts resulting in formation of unique bi- and tetranuclear complexes of 6-hydroxy-2,2′-bipyridines and 2-hydroxy-1,10-phenantrolines [9–11].

Derivatives of 3-pyridyl-1,2,4-triazine have attracted much attention because of their applications connected with their coordination properties and/or biological activity. 5,6-Diaryl-3-(2-pyridyl)-1,2,4-triazines give colored complexes with some transition metals (Fe, Co), that finds an application in analytical chemistry [12]. Alkyl derivatives of pyridyltriazines are extensively used as extracting reagents for the separation of lanthanides and actinides in the management of nuclear wastes [13,14]. Ru(II) complexes of pyridyltriazines are described as DNA structure probes [15,16]. Pt^{II} complexes of substituted 3-(2-pyridyl)-1,2,4-triazines possess HIV-1 antiviral activity [17,18]. 6-Aryl-3-pyridyl-1,2,4-triazine-5-ones significantly increase the formation of low-density lipoprotein (LDL) receptor protein, that is the origin of the genetic disease familial hypercholesterolemia [19,20]. At the same time, high reactivity of 1,2,4-triazines towards nucleophiles facilitates the synthesis of various functionalized derivatives [21,22].

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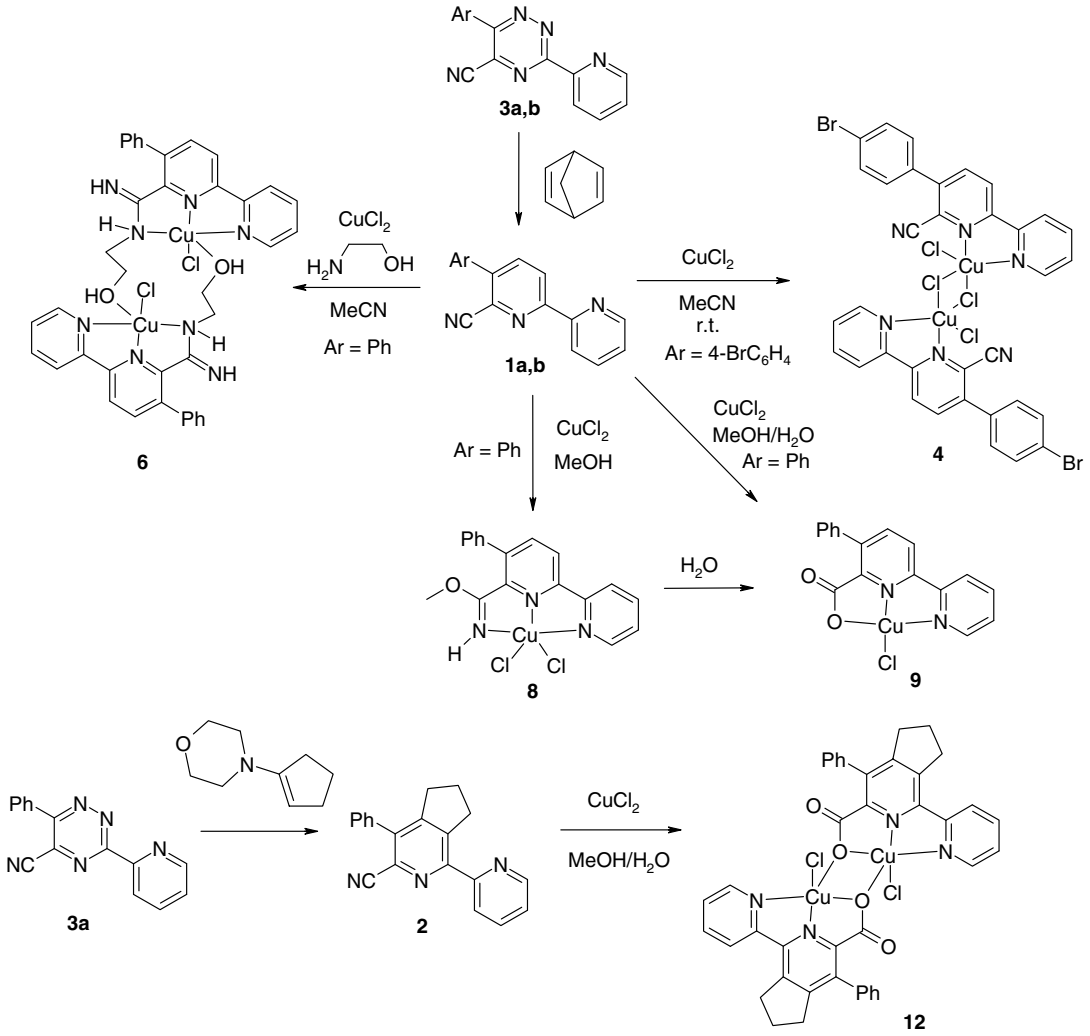
Here, we describe a reactivity of 3-pyridyl-1,2,4-triazines bearing cyano or phenylethynyl groups at the position 5 in comparison with that of corresponding 6-cyano-2,2′-bipyridines and 6-phenylethynyl-2,2′-bipyridine in Cu(II) activated reactions with some nucleophiles: water, methanol and ethanolamine.

2. Results and discussion

6-Cyano-2,2′-bipyridines (**1a,b** and **2**) were obtained from 5-cyano-3-(2-pyridyl)-1,2,4-triazines (**3a,b**) in the aza Diels–Alder reactions with 2,5-norbornadiene and 1-morpholinocyclopentene (Scheme 1) [23]. The nitrile group in cyanobipyridines **1, 2** exhibits extremely high resistance towards nucleophiles. We try to carry out reactions of cyanobipyridines with hydroxides, alkoxides, hydrazine, amines without any success – unchanged starting materials were isolated from reactional mixtures. Hydrolysis of the nitrile group was achieved only after refluxing in 50% sulfuric acid yielding bipyridine carboxamide. The reason of low reactivity of the nitrile group is that it is shielded from a nucleophilic attack by lone pair of the nitrogen atom of the pyridine ring from one side, and by the aryl substituent from another side. We decided to use Cu^{II} coordination to increase reactivity of cyanobipyridines **1**, **2**. In the absence of any nucleophile cyanobipyridines form typical for bipyridines complexes. For example bipyridine **1b** reacts with $CuCl_2 \cdot 2H_2O$ in acetonitrile solution yielding complex $[Cu_2(\mathbf{1b})_2Cl_4]$ (**4**) without chemical transformations of the ligand molecule (Scheme 1). Single crystals of the complex **4** suitable for X-ray diffraction were grown from acetonitrile. The molecular structure of **4** is shown in Fig. 1. The complex **4** is centrosymmetric dimer with two bridging chlorine atoms. Influence of the cyano group in this case is just slight steric hindrances resulting in distortion square pyramidal coordination of every Cu^{II} atoms in the complex **4**.

Addition of ethanolamine to the mixture of cyanobipyridine **1a** and copper(II) chloride in acetonitrile at room temperature results in metallocyclic complex $[Cu_2(\eta_3\text{-}\mu_2\text{-}\mathbf{5})_2Cl_2]^{2+}(Cl^-)$ $[CuCl_2]^-$ (**6**), where **5** is *N*-(2-hydroxyethyl)-5-phenyl-2,2′-bipyridine-6-carboxamidine (Scheme 1,



Scheme 1.

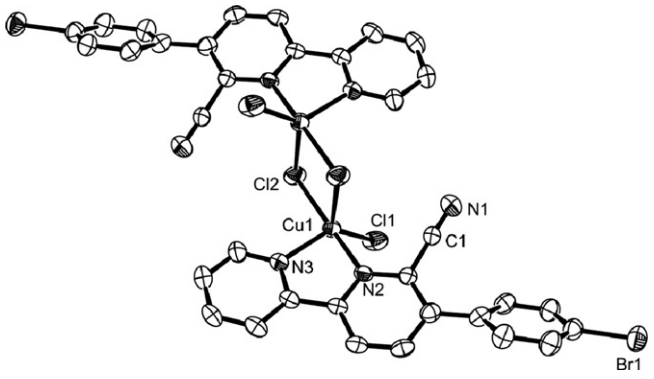


Fig. 1. ORTEP view on **4** (solvent molecule and hydrogens are omitted). Selected bond lengths (Å) and angles (°): Cu(1)–N(2) 2.011(2), Cu(1)–N(3) 2.041(2), Cu(1)–Cl(1) 2.2356(8), Cu(1)–Cl(2) 2.2427(7), Cu(1)–Cl(2a) 2.6593(8), N(2)–Cu(1)–N(3) 80.41(9), N(3)–Cu(1)–Cl(2) 97.06(7).

Fig. 2). It should be underlined that in the absence of the metal salt no reaction was observed after long-time heating under reflux of cyanobipyridine **1a** with ethanolamine in acetonitrile. Indeed the copper(II) coordination increases reactivity of the nitrile group dramatically. Obvious reason is that the bipyridine moiety in the complex like **4** is more electronegative if compare with free ligand. As expected ethanolamine reacts with the activated nitrile as N-nucleophile resulting in formation of the amidine **5**. Formation of the metallocyclic dimer $[Cu_2(\eta_3\text{-}\mu_2\text{-}\mathbf{5})_2Cl_2]^{2+}$ is result of the replacement of the chloride anion with hydroxyl of the ethanolamine moiety from coordination sphere of copper(II) atom of the next chelate. Every copper atom of the cycle has distorted square pyramidal coordination.

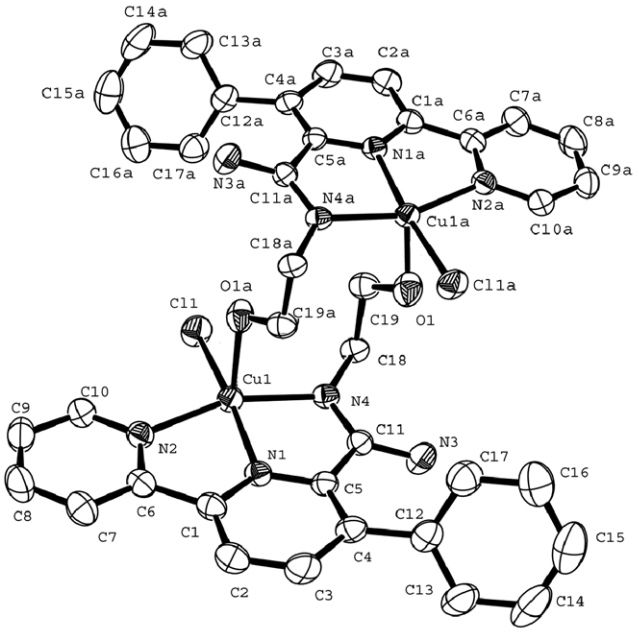


Fig. 2. ORTEP view on $[Cu_2(\eta_3\text{-}\mu_2\text{-}\mathbf{5})_2Cl_2]^{2+}$ (hydrogens are omitted). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.9454(16), Cu(1)–N(2) 2.0361(19), Cu(1)–N(4) 1.9957(18), Cu(1)–Cl(1) 2.2145(6), Cu(1)–O(1a) 2.3212(18), N(1)–Cu(1)–N(2) 79.59(7), N(1)–Cu(1)–N(4) 80.22(7).

The presence of copper(II) chloride activates addition of *O*-nucleophiles to the cyanobipyridine **1a** as well. While cyanobipyridine remains unchanged after long term refluxing in MeOH, the presence of $CuCl_2$ yields complex $[Cu(\mathbf{7})Cl_2]$ (**8**) containing *O*-methyl-5-phenyl-2,2′-bipyridine-6-carboxyimidate (**7**) as a ligand (Scheme 1). Single crystals of **8** were obtained by slow evaporation of the solvent from methanolic solution. The molecular structure of **8** is shown in Fig. 3, and selected bond distances are given in the caption.

Carboximidate in the complex **8** is quite sensitive towards hydrolysis. An attempt on recrystallization of **8** from water yielded complex [Cu(**9**)Cl] (**10**) with 5-phenyl-2,2′-bipyridine-6-carboxylate (**9**) as ligand (Scheme 1). Single-crystal X-ray diffraction studies of the complex **9** revealed molecular structure shown in Fig. 4. Molecules of **10** are self-organized into chains due to intermolecular chlorine–copper (distance Cl(2)–Cu(1a) is 3.115 Å) and copper–oxygen (distance Cu(1)–O(2a) is 3.151 Å) interactions (crystal packing of **10** see on Fig. S1, supplementary information).

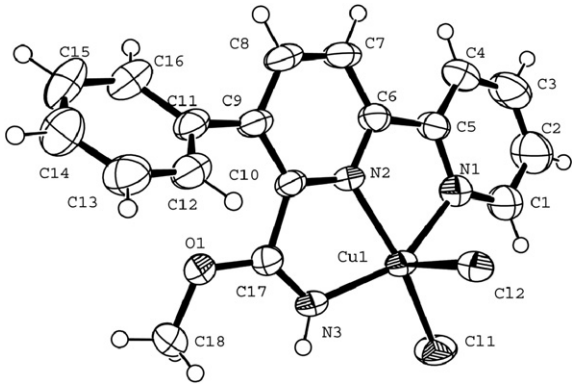


Fig. 3. ORTEP view of **8**. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.056(2), Cu(1)–N(2) 1.9851(19), Cu(1)–N(3) 2.018(2), Cu(1)–Cl(1) 2.2242(8), Cu(1)–Cl(2) 2.5395(9), N(1)–Cu(1)–N(2) 78.96(9), N(2)–Cu(1)–N(3) 78.45(9).

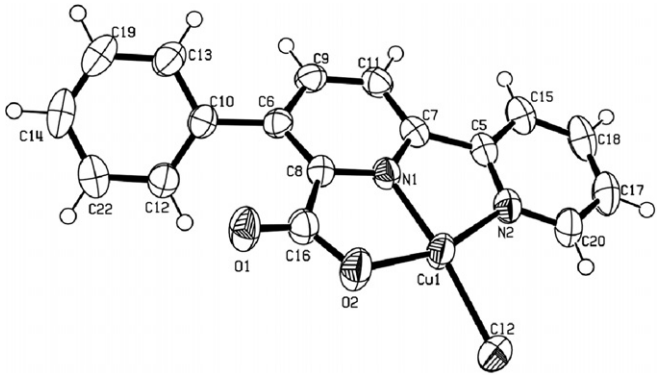
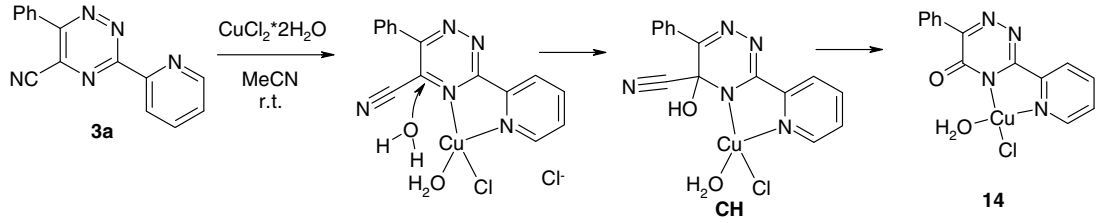


Fig. 4. ORTEP view on **10**. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.9269(12), Cu(1)–N(2) 2.0115(12), Cu(1)–Cl(2) 2.2137(4), Cu(1)–O(2) 1.9543(11), N(1)–Cu(2)–N(2) 81.04(5), N(1)–Cu(2)–O(2) 81.04(5).



Scheme 2. Formation of the complex **14**.

The same complex **10** was obtained by refluxing cyanobipyridine **1a** in the mixture of $MeOH/H_2O$ in the presence of copper(II) chloride (Scheme 1). It clearly shows that formation of a complex with metal cation, i.e. Cu^{2+}, increases dramatically reactivity of the practically inert towards nucleophilic attack cyanobipyridine **1**.

Hydrolysis of the cyanocyclopentenopyridine **2** was carried out under the same conditions yielding complex $[Cu_2(\mathbf{11})_2Cl_2]$ (**12**), where **11** is 5-phenyl-2-(2-pyridyl)-cyclopenteno[*c*]pyridine-6-carboxylate (Scheme 2). An ORTEP view of the complex **12** is given in Fig. 5, while selected bond distances and angles are given in the caption. Geometry of the ligand molecule is very similar to the ligand in the complex **9** in exception of the annelated cyclopentene, but the complex **12** is a dimer. Every copper(II) atom has distorted square planar coordination, Cu–Cu distance is 3.223 Å.

We decided to compare reactivity of cyanobipyridines **1** and the parent cyanotriazines **3** in reactions with nucleophiles in the presence of $CuCl_2$. In the absence of the metal salt an acetonitrile solution of the cyanotriazine **3** remains unchanged for a long period exactly like cyanobipyridine **1**. However an attempt to obtain simple complex of the cyanotriazine **1a** with $CuCl_2$ resulted in formation of a complex [Cu(**13**)(H_2O)Cl] (**14**), containing anion of 6-phenyl-3-(2′-pyridyl)-1,2,4-triazin-5-one **13** as ligand. So the metal salt initiates reaction of nucleophilic *substitution* of the cyano group (Scheme 2). The reaction proceeds under very mild condition: room temperature, dry acetonitrile. Source of reactive water is coordination sphere of copper(II) chloride hydrate only.

An ORTEP view of **14** is given in Fig. 6, while selected bond distances and angles are given in the caption. There are two independent molecules in the unit cell, whose geometries are very similar (Fig. S3, supplementary information). The Cu^{II} atom adopts a square planar geometry. As shown by the crystal packing (Fig. 7), the molecules are self-organized by extensive intermolecular hydrogen bonds between the coordinated water molecule and nitrogen of the triazine (O–H···N) of the adjacent molecules, with obvious directionality and short intermolecular contact between successive nitrogen and oxygen atoms [the distance N(3A)–O(1w) is 2.818 Å, the angle N(3A)–O(1w)–O(1) is 109.62°], therefore a polymeric one-dimensional chain results. Moreover, complexes **14** form columns along the axis *c* due to intermolecular Cu–Cl interaction (measured distance Cu(1)–Cl(1A) is 3.159 Å) (Fig. S2, supplementary information). Additional intermolecular contacts through oxygen of the carbonyl and Cu^{II} are also evident (distance Cu(1)–O(1A) is 3.375 Å).

Two questions need answers: why the reaction proceeds so easily and what the reason of the metal co-ordination through N-4 atom of the 1,2,4-triazine instead of N-2 while in all known (database of Cambridge Crystallographic Data Centre) metal complexes of 3-pyridyl-1,2,4-triazines

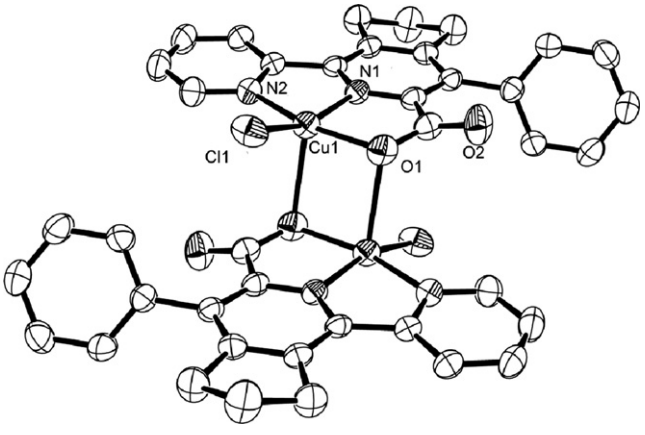


Fig. 5. ORTEP view on **12** (hydrogens are omitted). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.9294(16), Cu(1)–N(2) 2.0106(17), Cu(1)–Cl(1) 2.2063(6), Cu(1)–O(1) 1.9716(15), Cu(1)–O(1a) 2.451, Cu(1)–Cu(1a) 3.223, N(1)–Cu(1)–N(2) 80.27(7), N(1)–Cu(1)–O(1) 99.80(7).

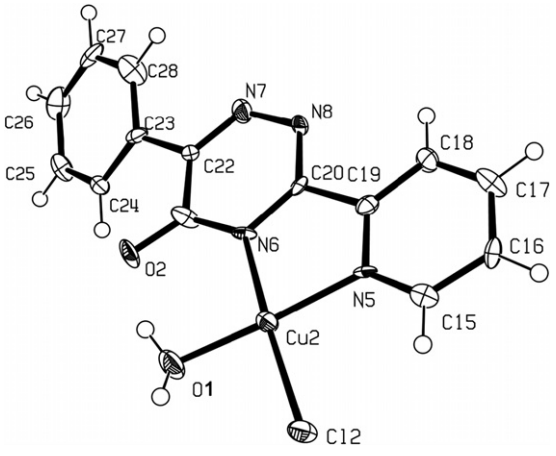


Fig. 6. ORTEP view on **14**. Selected bond lengths (Å) and angles (°): Cu(2)–N(6) 2.038(7), Cu(2)–N(5) 1.990(7), Cu(2)–O(1) 1.946(7), Cu(2)–Cl(2) 2.264(2), N(6)–Cu(2)–N(5) 82.6(3), N(6)–Cu(2)–O(1) 91.2(3), N(5)–Cu(2)–Cl(2) 95.7(2).

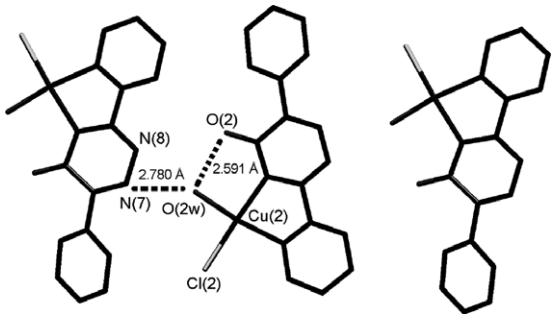
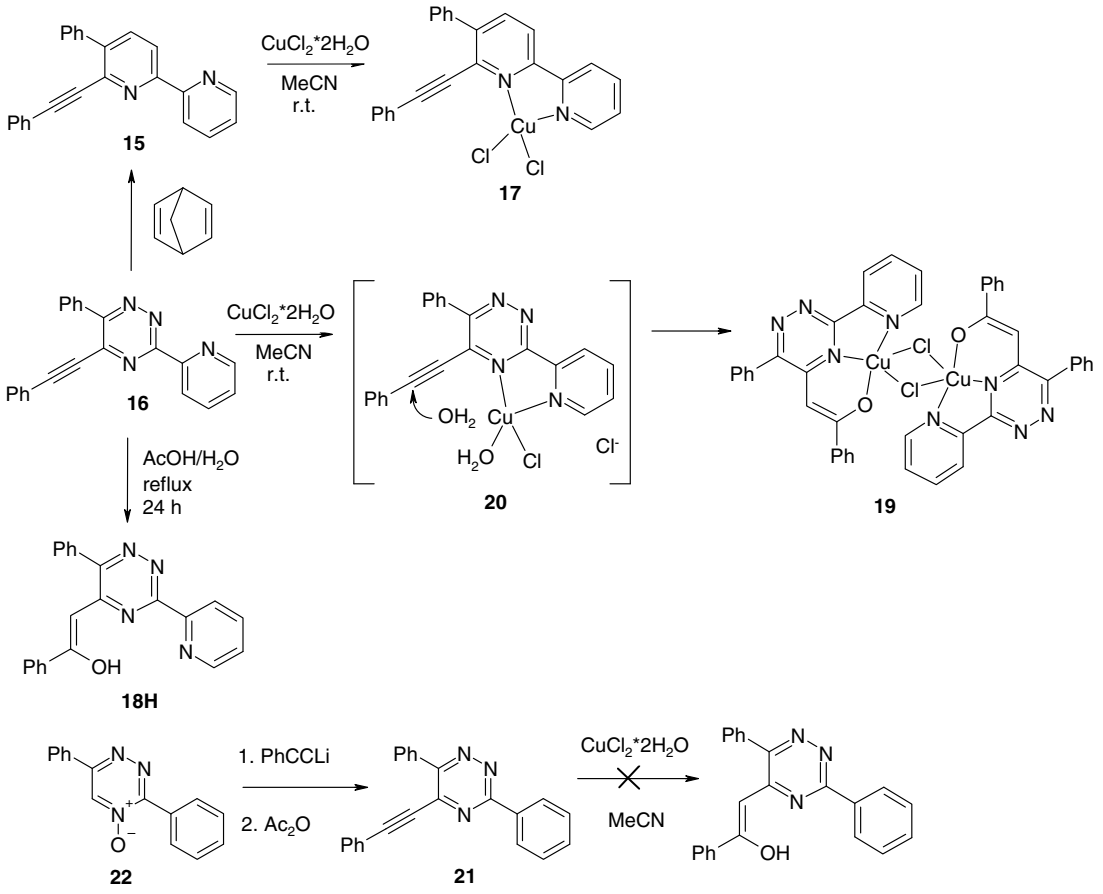


Fig. 7. Intra- and intermolecular H-bonds resulting in a chain formation in crystal of **14**.

coordinations through N-2 were reported. To explain it we suggested following mechanism of the reaction. It is known, that coordination of a heterocycle to a metal ion has an effect similar to quaternization and consequently activates the α-carbon atom of the heterocycle to be attacked by a nucleophilic water to form a covalent hydrate (**CH**) [24]. In the pyridyltriazine **3a** only N-4 coordination leads to sufficient activation of C-5 to nucleophilic attack, that explains unusual regioselectivity of the coordination in the product **14**. Additional acceleration of the reaction is due to a transport of the water molecule from the coordination sphere of $CuCl_2 \cdot 2H_2O$ close to the reactional center of the activated heterocycle. Elimination of the cyanide anion from hydrate **CH** resulted in the complex **14** (Scheme 2).

1,2,4-Triazine ring is more π-deficient in comparison with pyridine ring, so triazines are more active in reactions with nucleophiles than analogous pyridines. The same influence of the number of nitrogen atoms in a heterocycle is observed for corresponding Cu^{II} complexes. We examined this thesis in hydration reaction of acetylene moiety attached at α-position of pyridine or 1,2,4-triazine. 6-Phenylethynyl-2,2′-bipyridine **15** was obtained from 5-phenylethynyl-3-(2-pyridyl)-1,2,4-triazine **16** in the aza Diels–Alder reactions with 2,5-norbornadiene (Scheme 3) [25]. It was found that ethynylbipyridine **15** is indifferent towards water neither at room temperature no after long term heating at reflux in the mixture $MeCN/H_2O$. Addition of copper(II) chloride to the reactional mixture has no any effect on the hydration reaction. The single product isolated was complex $[Cu(\mathbf{15})Cl_2]$ (**17**) without any transformation of the ligand **15** (see Fig. 8).

Ethynyltriazine **16** is much more susceptible towards nucleophilic attack. Thus 1 day heating under reflux of triazine **16** in the $AcOH/H_2O$ mixture yields 5-phenacyl-6-phenyl-3-(2-pyridyl)-1,2,4-triazine (**18H**) (Scheme 3). Reactivity of ethynyltriazine **16** increases dramatically in the presence of $CuCl_2 \cdot 2H_2O$. The Cu^{II} activated hydration reaction proceeds at room temperature in dry acetonitrile



Scheme 3. Reactions of acetylene derivatives.

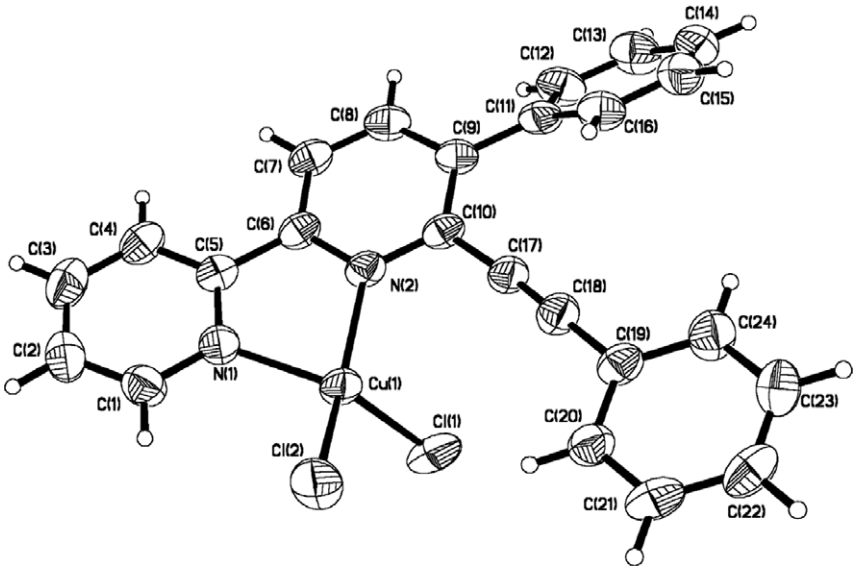


Fig. 8. ORTEP view on **17**. Selected bond lengths (Å): Selected bonds length, (Å): Cu(1)–Cl(1) 2.2296(12), Cu(1)–N(1) 2.011(3), Cu(1)–N(2) 1.992(2), C(17)–C(18) 1.196(5).

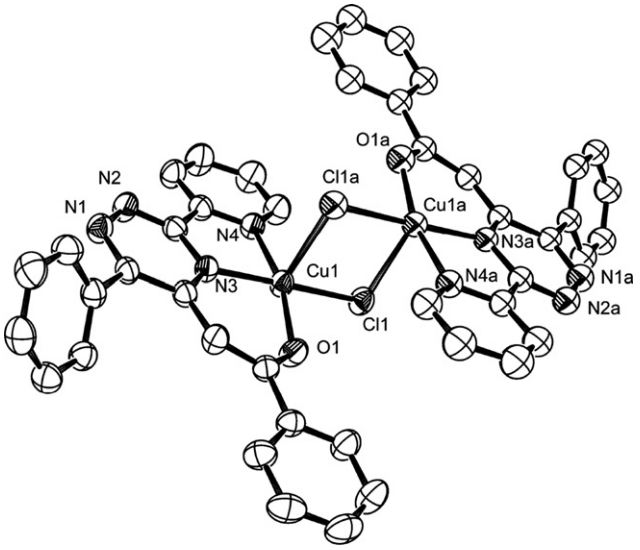


Fig. 9. ORTEP view on **19**. Selected bond lengths (Å) and angles (°): Cu(1)–N(3) 1.976(2), Cu(1)–N(4) 2.017(2), Cu(1)–O(1) 1.917(2), Cu(1)–Cl(1) 2.2626(8), Cu(1)–Cl(1a) 2.7116(9), N(3)–Cu(1)–N(4) 81.82(10), N(3)–Cu(1)–O(1) 91.18(9).

without excess of water except coordination water of copper(II) chloride hydrate yielding $[Cu_2(\mathbf{18})_2Cl_2]$ (**19**) containing anion of phenacyltriazine **18** as ligand (Scheme 3). The binuclear complex **19** is centrosymmetric dimer with bridging chlorides and square pyramidal co-ordination of each Cu^{II} (Fig. 9).

Obviously formation of the intermediate complex **20** is a key step of this reaction. Any substituent preventing formation of such complex should decrease significantly reactivity of ethynyltriazine. To confirm this suggestion we obtained 3,6-diphenyl-5-phenylethynyl-1,2,4-triazine (**21**) by reaction of 3,6-diphenyl-1,2,4-triazine 4-oxide (**22**) with lithium phenylacetylene (Scheme 3). Triazine **21** is unable to form complex with a metal cation. As result, acetylene **20** does not undergo any reaction in acetonitrile solutions in the presence of $CuCl_2 \cdot 2H_2O$.

3. Conclusions

Cyano- and ethynyl-1,2,4-triazines are more active in reactions with nucleophiles if compare with cyano- and ethynylbipyridines. Actually, cyanobipyridines do not react with nucleophiles without additional activation. Formation of Cu^{II} complexes accelerates these reactions dramatically both for triazines and bipyridines. Transition metal activation is only method towards derivatives of 6-cyano-5-aryl-2,2′-bipyridines.

4. Experimental

All solvents were purified by standard methods prior to use. Commercially available chemicals were used without further purification. Cyanotriazines **3** [26], phenylethynyltriazine **16** and phenylethynyl-2,2′-bipyridine **15** [25], cyano-2,2′-bipyridines **1, 2** [26], 3,6-diphenyltriazine 4-oxide **22** [27] were prepared by methods published elsewhere. Melting points are uncorrected. NMR spectra were recorded on a 400 MHz Bruker Avance DRX spectrometer. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer.

4.1. Synthesis of complexes *4, 14* and *19*

Solution of ligand **1b, 3a** or **16** (0.15 mmol) in acetonitrile (15 mL) was added to solution of copper chloride dihydrate (26 mg, 0.15 mmol) in acetonitrile (15 mL). Resulting dark brown solution was kept for 3 day at r.t. Appeared crystals were filtered off.

Complex **4**: Dark-green crystals. Yield 70%. Anal. Calc for $C_{17}H_{10}N_3BrCl_2Cu$ (472.66): C, 43.20; H, 2.56; N, 16.91. Found: C, 43.41; H, 2.32; N, 16.99%.

Complex **14**: Dark-green crystals. Yield 65%. Anal. Calc. for $C_{14}H_{11}ClCuN_4O_2$ (366.26): C, 45.91; H, 3.03; N, 15.30. Found: C, 45.71; H, 3.05; N, 15.00%.

Complex **19**: Dark-green crystals. Yield 80%. Anal. Calc. for $C_{44}H_{30}N_8O_2Cl_2Cu_2$ (900.74): C, 58.67; H, 3.36; N, 12.44. Found: C, 58.51; H, 3.32; N, 12.27%

4.2. Synthesis of complex *8*

Solution of ligand **1a** (39 mg, 0.15 mmol) in methanol (15 mL) was added to solution of copper chloride dihydrate (26 mg, 0.15 mmol) in methanol (15 mL). Resulting mixture was stirred under reflux for 1 day to give green solution. The solution was cooled down and condensed slowly for some days. Resulting green crystals were filtered off. Yield 70%. Anal. Calc. for $C_{72}H_{62}Cl_8Cu_4N_{12}O_5$ (1713.10): C, 50.48; H, 3.65; N, 9.81. Found: C, 50.60; H, 3.41; N, 9.80%.

4.3. Synthesis of complex *6*

Solution of ligand **1a** (39 mg, 0.15 mmol) and ethanolamine (0.30 mmol) in boiling acetonitrile (15 mL) was added to solution of copper chloride dihydrate (51 mg, 0.30 mmol) in acetonitrile (15 mL) at 80 °C. Green precipitate was formed. The mixture was stirred under reflux for 1 hour to give dark green solution. The solution was cooled down and condensed slowly for some days. Resulting dark-green crystals were filtered off. Yield 65%. Anal. Calc. for $C_{40}H_{44}Cl_5Cu_3N_8O_4$ (1068.70): C, 44.95; H, 4.15; N, 10.48. Found: C, 44.99; H, 4.11; N, 10.20%.

4.4. Synthesis of complexes *10* and *12*

Solution of ligand **1a** or **2**(0.15 mmol) in hot methanol (15 mL) was added to solution of copper chloride dihydrate (26 mg, 0.15 mmol) in water (30 mL). Resulting mixture was stirred under reflux for 1 day to give blue solution. The solution was condensed in vacuo in half and then cooled down. Some days later appeared dark-blue crystals were filtered off.

Complex **10**: Dark-blue crystals. Yield 85%. Anal. Calc. for $C_{17}H_{11}ClCuN_2O_2$ (374.27): C, 54.55; H, 2.96; N, 7.48. Found: C, 54.60; H, 3.01; N, 7.20%.

Complex **12**: Dark-blue crystals. Yield 90%. Anal. Calc. for $C_{40}H_{30}Cl_2Cu_2N_4O_4$ (828.68): C, 57.97; H, 3.65; N, 6.76. Found: C, 57.60; H, 3.42; N, 6.86%.

4.5. Synthesis of 5-phenacyl-6-phenyl-3-(2-pyridyl)-1,2,4-triazine 18H

5-Ethynyl-1,2,4-triazine **16** (332 mg, 1 mmol) was dissolved in acetic acid (10 mL) with water (1 mL), and was heated with reflux for 24 h. Then solvent was removed, the residue was treated with acetonitrile (5 mL), and yellow solid was filtered off. The product was recrystallized from toluene to give phenacyltriazine **18H**. Yield 45%. M.p.: 156 °C. ^{1}H NMR ($CDCl_3$), δ: 6.25 (s, 1H, COC*H*), 7.48–7.80 (m, 11H, $H_{aromatic}$ + H-5′), 8.14 (m, 1H, H-4′), 8.54 (m, 1H, H-3′), 8.95 (m, 1H, H-6′), 15.39 (br.s, 1H, NH). Anal. Calc. for $C_{22}H_{16}N_4O$ (352.38): C, 74.98; H, 4.58; N, 15.90. Found: C, 74.79; H, 4.47; N, 15.86%.

4.6. Synthesis of complex *17*

Solution of ligand **15** (50 mg, 0.15 mmol) in acetonitrile (30 mL) was added to a solution of $CuCl_2{}^*2H_2O$ (26 mg, 0.15 mmol) in acetonitrile (30 mL). The resulting dark brown solution was kept for 3 days at r.t. Appeared dark-green crystals were filtered off. Yield 88%. Anal. Calc. for $C_{24}H_{16}Cl_2CuN_2$ (466.86): C, 61.75; H, 3.45; N, 6.00. Found: C, 61.52; H, 3.62; N, 6.28%.

4.7. Synthesis of 3,6-diphenyl-5-phenylethynyl-1,2,4-triazine (*21*)

Solution of lithium phenylacetylide, prepared by addition of 1.6 M butyllithium in hexane (0.66 mL, 1.05 mmol) to solution of phenylacetylene (0.11 mL, 1 mmol) in 10 ml of THF, was added with stirring to solution of 1,2,4-triazine 4-oxide **22** (250 mg, 1 mmol) in THF (10 ml) at −40 °C under argon, and the mixture was kept at this temperature for 20 min. Acetic anhydride (0.1 mL, 1.05 mmol) was added at the same temperature, and the reactional mixture was allowed to warm up to room temperature. Then the solvent was removed under reduced pressure, the residue was dissolved in chloroform and phenylethynyltriazine **21** was isolated by column chromatography (silica gel, CH_2Cl_2). Analytical sample was recrystallized from acetonitrile. Yield, 85%. M.p. 175 °C (from acetonitrile). ^{1}H NMR ($CDCl_3$), δ: 7.38–7.58 (m, 11H), 8.17 (m, 2H), 8.63 (m, 2H). ^{13}C NMR ($CDCl_3$), δ: 86.38, 99.57, 120.74, 128.37, 128.64, 128.85, 129.29, 130.38, 130.56, 131.70, 132.53, 134.09, 134.38, 141.85, 156.62, 161.39. HRMS (EI): $C_{23}H_{15}N_3$ requires M^+, 333.1266, found 333.1254.

4.8. X-ray crystallography

Diffraction data of complexes **4**, **6**, **8**, **10**, **12**, **14, 17** and **19** were collected on a *Xcalibir 3 CCD* diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Details of X-ray crystallography for every compound are given in the Table 1. Analytical numeric absorption correction is applied using a multifaceted crystal model. The structure is solved by direct method and refined anisotropically with SHELX-97 program package [28]. The coordinates of non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in calculations isotropically but not refined.

Table 1
Details of X-ray crystallography

Complex	4	6	8	10	12	14	17	19
Empirical formula	$C_{36}H_{23}Br_2Cl_4Cu_2N_7$	$C_{40}H_{44}C_{15}Cu_3N_8O_4$	$C_{72}H_{62}Cl_8Cu_4N_{12}O_5$	$C_{17}H_{11}ClCuN_2O_2$	$C_{40}H_{30}Cl_2Cu_2N_4O_4$	$C_{14}H_{11}ClCuN_4O_2$	$C_{24}H_{16}N_2Cl_2Cu$	$C_{44}H_{30}Cl_2Cu_2N_8O_2$
Formula weight	982.31	1068.70	1713.10	374.27	828.68	366.26	466.83	900.74
Temperature, K	295(2)	295(2)	293(2)	295(2)	295(2)	120(2)	293(2)	220(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*P*2/*c*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*c*	$P\bar{1}$	$P\bar{1}$
A (Å)	18.6465(9)	9.8484(4)	9.5697(5)	12.6928(6)	9.1083(3)	23.924(7)	9.114(2)	9.1197(7)
B (Å)	9.1640(2)	9.4152(5)	11.9757(5)	15.7460(7)	20.1698(7)	14.882(5)	10.008(2)	9.7936(8)
C (Å)	21.9563(11)	23.8563(9)	17.4427(7)	7.3556(3)	9.4923(4)	7.987(2)	12.397(3)	12.0090(10)
A (°)	90	90	83.547(3)	90	90	90	112.34(3)	113.375(2)
B (°)	90.469(4)	95.209(3)	79.286(4)	91.613(4)	101.031(3)	99.028(13)	102.08(3)	102.581(2)
γ (°)	90	90	70.165(4)	90	90	90	92.20(3)	91.994(2)
Volume (Å^3)	3751.7(3)	2202.93(17)	1845.00(14)	1469.51(11)	1711.64(11)	2808.7(15)	1014.0(4)	952.07(13)
Z	4	2	1	4	2	8	2	1
ρ_{calc} (g/cm^3)	1.739	1.611	1.542	1.692	1.608	1.732	1.529	1.571
M (mm^{-1})	3.586	1.789	1.486	1.678	1.449	1.757	1.353	1.309
F(000)	1936	1088	870	756	844	1480	474	458
θ Range (°)	2.64–31.72	2.76–26.38	n/a	3.05–31.72	2.98–26.37	n/a	12.1–14.15	0.542–0.988
Reflections collected	21931	12034	28451	20747	6350	17343	4631	7090
Independent reflections ($R_{(int)}$)	5833 (0.0726)	4449 (0.0280)	12456 (0.0427)	4553 (0.0316)	3396 (0.0152)	5445 (0.0756)	2066 (0.0156)	3884 (0.0270)
Parameters	241	288	487	208	235	413	262	262
R [$I > 2\sigma(I)$]	$R_1 = 0.0411$, $wR_2 = 0.0794$	$R_1 = 0.0309$, $wR_2 = 0.0635$	$R_1 = 0.0411$, $wR_2 = 0.0794$	$R_1 = 0.0298$, $wR_2 = 0.0572$	$R_1 = 0.0281$, $wR_2 = 0.0677$	$R_1 = 0.0884$	$R_1 = 0.0336$, $wR_2 = 0.0768$	$R_1 = 0.0484$, $wR_2 = 0.1199$
R (all data)	$R_1 = 0.0892$, $wR_2 = 0.0849$	$R_1 = 0.0501$, $wR_2 = 0.0664$	$R_1 = 0.0411$, $wR_2 = 0.0794$	$R_1 = 0.0720$, $wR_2 = 0.0611$	$R_1 = 0.0429$, $wR_2 = 0.0708$	$R_1 = 0.2555$, $wR_2 = 0.2670$	$R_1 = 0.1531$, $wR_2 = 0.0996$	$R_1 = 0.0592$, $wR_2 = 0.1265$
Goodness of fit	1.000	1.006	1.012	1.000	1.000	0.999	1.001	1.000

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Appendix A. Supplementary material

CCDC 290967, 664380, 664381, 664382, 664383, 664384, 664385 and 664386 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.02.016.

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