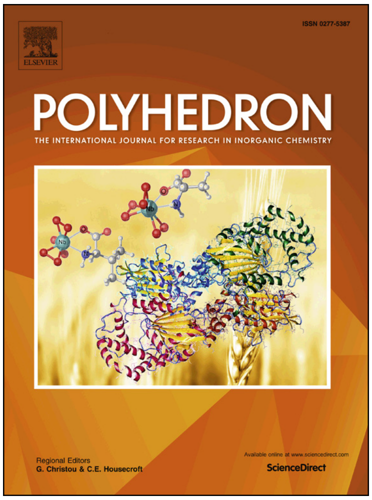

Synthesis, crystal structure and investigation of the catalytic and spectroscopic properties of a Zn(II) complex with Coumarin-hydrazone ligand

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Synthesis, crystal structure and investigation of the catalytic and spectroscopic properties of a Zn(II) complex with Coumarin-hydrazone ligand

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Abstract

A Zn(II) complex with coumarin-hydrazone ligand, $[ZnCl(HL)(CH_3OH)_{0.76}(H_2O)_{0.24}]\cdot 0.24(CH_3OH)$ (**1**), was synthesized from the reaction of equimolar amount of $ZnCl_2\cdot 4H_2O$ and (*E*)-2-hydroxy-*N*'-(1-(2-oxo-2H-chromen-3-yl)ethylidene)benzohydrazide (**H_2L**) in methanol solvent. The complex was characterized by elemental analysis, spectroscopic methods and single crystal X-ray diffraction studies. Single crystal X-ray analysis indicated that the Zn(II) ion in complex **1** has a distorted square pyramidal environment and the coumarin-hydrazone ligand is coordinated as a mononegative tridentate ONO-donor ligand, $(HL)^-$. The photoluminescent studies indicated that complex **1** has emission at about 470 nm. The catalytic potential of complex **1** was investigated for preparing tetrazole based compounds from the azide-nitrile cycloaddition reactions. The catalytic reactions were carried out in water as a green solvent. The results indicated that complex **1** is an active catalyst for preparing tetrazole compounds. The effects of temperature and electronic properties of the substituent connected to the nitrile group on the activity of this catalytic system were also considered.

Keywords: Zn(II) complex; Crystal structure; Coumarin-hydrazones; Catalytic properties; Spectroscopic studies

1. Introduction

Zinc, as the second most abundant metal ion the human body, is an important bioessential trace element which has been recognized as a crucial element in a large number of proteins and enzymes [1]. Zinc plays vital roles in several biological processes (like gene expression, metabolism of cells, apoptosis, etc.) and it is responsible for some neurological disorders like Parkinson and Alzheimer diseases [2]. Due to this, specific detection of zinc ion has attracted considerable attention during recent years and a number of methods have been developed for Zn detection [3]. Among these methods, fluorescence spectroscopy by the use of fluorescent chemosensors has been introduced as one of the advanced techniques for detection of Zn(II) ion which is also known as low cost, high selective and sensitive method [4]. Fluorescence properties of zinc(II) complexes, especially in the function of light-emitting materials (LEDs), have been intensively explored and the results indicate that the fluorescence intensity and properties of Zn(II) complexes are sensitive to the structure and donor/acceptor potentials of the employed organic ligands [5]. As catalyst, zinc complexes have been frequently used in phenol oxidation [6], CO_2 fixation [7], ring opening polymerization [8], Friedel-Crafts acylation [9] and 3+2 nitrile-azide cycloaddition reactions [10].

Tetrazoles are a class of important five membered nitrogen rich heterocyclic compounds which contain one carbon and four nitrogen atoms [11]. Although such heterocyclic systems are not found in nature, they show broad range of biological and pharmaceutical activities [12]. By having low toxicity and high lipophilicity, tetrazoles have been used as clinical drugs [13], HIV-inhibitors [14], anti-inflammatories [15], antibiotics [16] and antimicrobial compounds [17]. Furthermore, tetrazoles have also been used as explosives and gas-generating materials [18] and they have been employed as important synthons in synthetic organic chemistry [19]. In inorganic and organometallic chemistry, tetrazoles have been utilized as efficient ligands for the formation of interesting multinuclear complexes and coordination polymers [20]. Due to widespread applications of tetrazoles, their preparation has been the subject of intense investigation and several methods and catalytic systems have been introduced for production of tetrazoles. Among the various reported methods in literature, the 3+2 cycloaddition reaction of a nitrile with azide in the presence of a catalyst is the most common and conventional method to synthesize a tetrazole ring [21]. The results of studies indicated that the zinc based compounds are more effective catalysts for production of tetrazoles. It is expected that the development of new zinc based catalysts for 3+2 azide-nitrile cycloaddition reactions can lead to new effective catalytic systems for preparing this class of heterocyclic compounds.

Coumarins are a class of heterocyclic compounds which display important biological activities and have been observed in many plants [22]. Recently, it has been reported that the coumarin Schiff-base derivatives are effective fluorescent chemosensors for Zn(II) [23]. Some of the coumarin derivatives, like 3-acetylcoumarins, have high potential to be used in coordination chemistry by the reaction with suitable amines to form interesting Schiff base ligands [24]. Coumarin-hydrazone Schiff base ligands, obtained from the reaction of 3-acetylcoumarin with hydrazones, can act as interesting tridentate ONO-donor ligands in preparing transition metal complexes. By considering the high stability of hydrazone complexes [25], coumarin-hydrazone complexes can be efficient and stable catalysts in various catalytic reactions. Moreover, some of the hydrazones have also shown good fluorescent properties [26]. Therefore, it is predictable that the combination of coumarin and hydrazone compounds can show interesting optical properties. However, considering literature including Cambridge Structural Database (CSD) indicates that they are less studied and there are only three reports about coumarin-hydrazone complexes [27]. Recently, we have also reported some transition metal complexes and coordination polymers with coumarin-naphthohydrazone ligand that showed a rare coordination mode in the formation of coordination polymers [28].

In this paper, we report synthesis, characterization, spectroscopic properties, crystal structure and catalytic activity of a Zn(II) complex with coumarin-hydrazone ligand.

2. Experimental

2.1. Materials and instrumentations

Zinc(II) chloride tetrahydrate, ethyl acetoacetate, salicylaldehyde, piperidine and acetic acid were purchased from Merck and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. 3-Acetylcoumarin was prepared according to previous report [28]. FT-IR spectra were recorded as KBr disks with a Bruker FT–IR spectrophotometer. UV–Vis solution spectra were recorded on a thermo-spectronic Helios Alpha spectrophotometer. The zinc content of the complex was measured by atomic absorption analysis using Varian Spectra AA-220 equipment. The elemental analyses (carbon, hydrogen and nitrogen) of the compounds were obtained from a Carlo ERBA Model EA 1108 analyzer. ^{1}H and ^{13}C NMR spectra in DMSO-d_6 solution were measured on a Bruker 250 MHz spectrometer and the chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). Thermogravimetric analysis was performed with a Mettler Toledo TGA-DSC instrument. Photoluminescence spectra of the ligand and complex were recorded on a Perkin-Elmer Luminescence Spectrometers (equipped with a xenon lamp) by absorption and emission modes. The spectra were recorded at room temperature in the range of 200–900 nm.

*2.2. Synthesis of (E)-2-hydroxy-N'-(1-(2-oxo-2H-chromen-3-yl)ethylidene)benzohydrazide (**H_2L**)*

A methanol solution (10 mL) of 3-acetylcoumarin (0.565 g, 3.0 mmol) was added to a methanolic solution of 2-hydroxybenzohydrazide (0.456 g, 3.0 mmol) and the solution was refluxed for 2 h at 70 °C. The obtained yellow solid was separated, filtered off and washed with cold methanol and finally recrystallized from ethanol. Yield: 92.0% (890 mg). *Anal.* Calc. for $C_{18}H_{14}N_2O_4$ (MW = 322.31): C, 67.07; H, 4.38; N, 8.69%. Found: C, 67.13; H, 4.32; N, 8.74%. FT-IR (KBr, cm^{-1}): 3400 (m, br), 3178 (m), 3161 (m), 3070 (m), 3052 (br, m), 3031 (br, m), 2950 (w), 2929 (w), 1735 (m), 1712 (m), 1690 (vs), 1609 (vs), 1603 (vs), 1576 (s), 1557 (vs), 1487 (s), 1456 (vs), 1409 (m), 1371 (m), 1334 (s), 1308 (s), 1297 (s), 1252 (w), 1230 (s), 1215 (s), 1159 (vs), 1140 (s), 1120 (s), 1092 (m), 1032 (m), 967 (m), 938 (s), 879 (w), 825 (w), 808 (w), 779 (s), 769 (vs), 754 (s), 737 (m), 699 (m), 629 (w), 597 (w), 554 (w), 541 (w), 535 (w), 529 (w), 492 (w), 461 (m), 413 (m). ^1H NMR (250.13 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 2.26$ (s, 3H, $-CH_3$), 6.80-7.01 (m, 3H, aromatic), 7.38-7.51 (m, 3H, aromatic), 7.64 (t, 1H, $J = 7.25$ Hz, aromatic), 7.85 (d, 1H, $J = 7.25$ Hz, aromatic), 8.26 (s, 1H), 11.24 (s, 1H, NH), 11.63 ppm (s, 1H, OH). ^{13}C NMR (62.90 MHz, DMSO-d_6): $\delta = 16.1$ ($-CH_3$), 116.5, 117.5, 118.2, 119.2, 119.7, 125.3, 129.7, 131.1, 132.9, 133.9, 142.2, 147.5, 150.4, 153.9, 157.6, 159.8 (C=O, ester), 162.9 ppm (C=O, amide). UV-Vis (in CH_3OH, $c = 2.5\times10^{-5}$ M, λ_{max} [nm] with ε [M^{-1} cm^{-1}]): 235 (41200), 360 (3400).

*2.3. Synthesis of complex $[ZnCl(HL)(CH_3OH)_{0.76}(H_2O)_{0.24}]\cdot0.24(CH_3OH)$ (**1**)*

Complex **1** was synthesized by the reaction of the ligand H_2L (0.322 g, 1.00 mmol) and $ZnCl_2\cdot4H_2O$ (0.208 g, 1.00 mmol) in methanol by using thermal gradient method in a branched tube. The above mentioned amounts of the materials were placed in the main arm of a branched tube. Methanol was carefully added to fill the arms, the tube was sealed and the reagents containing arm was immersed in oil bath at 60 °C, while the other arm was kept at ambient temperature. After twenty day, block yellow crystals were deposited in the cooler arm. Yield 86.4% (0.396 g). *Anal.* Calc. For $C_{19}H_{17.47}ClN_2O_{5.24}Zn$ (MW = 458.40): C, 49.77; H, 3.84; N, 6.11; Zn, 14.26. Found: C, 49.87; H, 3.80; N, 6.02; Zn, 14.20%. FT-IR (KBr, cm^{-1}): 3440 (m, br), 3059 (w), 2925 (w), 1666 (vs), 1607 (s), 1591 (s), 1560 (s), 1513 (s), 1496 (s), 1468 (s), 1454 (m), 1442 (m), 1371 (s), 1356 (m), 1335 (m), 1260 (s), 1218 (m), 1186 (s), 1165 (m), 1147 (w), 1124 (m), 1077 (m), 1034 (m), 979 (m), 966 (m), 929 (m), 860 (w), 838 (m), 828 (w), 764 (vs), 727 (w), 700 (m), 670 (m), 643 (m), 591 (m), 580 (m), 537 (m), 529 (w), 485 (m), 441 (w), 426 (m). ^1H NMR (250.13 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 2.28$ (s, 3H, $-CH_3$), 3.12 (s, 3H, $-OCH_3$), 6.92-7.89 (m, 8H, aromatic), 8.32 (s, 1H), 12.02 ppm (s, 1H, OH). ^{13}C NMR (62.90 MHz, DMSO-d_6): $\delta = 16.8$ ($-CH_3$), 49.0 ($-OCH_3$), 116.5, 117.2, 117.6, 118.0, 119.2, 119.7, 125.5, 129.8, 130.6, 133.4, 133.7, 134.4, 143.6, 147.4, 153.6, 159.2 (C=O, ester), 160.3 ppm (N=C−O). UV-Vis (in CH_3OH, $c = 2.5\times10^{-5}$ M, λ_{max} [nm] with ε [M^{-1} cm^{-1}]): 220 (45000), 310 (38000), 410 (30000).

2.4. Single crystal X-ray crystallography

Data collection for X-ray structure determination of complex **1** was performed on a Kuma R four-circle diffractometer with a Sapphire CCD detector using graphite monochromatized Mo*Kα* radiation. Data were collected at 100(1) K using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction and absorption corrections were carried out with the Xcalibur R software, CrysAlis^{Pro} [29]. The structure was solved by direct methods with SHELXS and refined by a full-matrix least-squares technique on F^2 using SHELXL-2016 [30] with anisotropic thermal parameters for the non-H-atoms. The H atoms were found in difference Fourier maps, but in the final refinement cycles they were repositioned in their calculated positions and refined using a riding model, with C–H = 0.95–0.99 Å, and with U_{iso}(H) = 1.2U_{eq}(CH) or 1.5U_{eq}(CH_3), except for the OH atoms, which were located in Fourier maps, refined isotropically and then were constrained to ride on their parent atoms (AFIX 3 instruction in SHELXL-2016). Two different ligands share the same coordination site in the complex molecule: CH_3OH (with s.o.f. = 0.76) and H_2O (with s.o.f. = 0.24) which in the case of H_2O a methanol molecule is also located beside the complex molecule. Thus, the crystals of complex **1** are generated from two different complex molecules, $[ZnCl(HL)(CH_3OH)]$ and $[ZnCl(HL)(H_2O)]\cdot CH_3OH$, and the formula $[ZnCl(HL)(CH_3OH)_{0.76}(H_2O)_{0.24}]\cdot 0.24(CH_3OH)$ in the final model corresponds to the existence of these two complexes, randomly occupying the crystallographic sites of the unit cell in a 0.76:0.24 ratio. The structure plots were prepared with DIAMOND [31]. Details of structure refinements are given in Table 1.

Table 1.

*2.4. Catalytic activity of complex **1** in preparation of tetrazole derivatives*

The catalytic reactions for production of tetrazole derivatives were carried out in a 25 mL round bottom flask at aerial atmosphere. For this purpose, sodium azide (2 mmol) was added to a flask and was dissolved in distillated water (5 mL). Then, the target benzonitrile derivative (1 mmol) was added to the flask. Finally, complex **1** (0.01−0.15 mmol) was added to the flask and the mixture was stirred at 90 °C. The progress of the reaction was monitored by thin-layer chromatography (TLC) until the starting benzonitrile was finished. After completion of the reaction, 1 mmol of diluted HCl was added drop-wise to the reaction mixture and simultaneously, white precipitates were slowly formed. After completion of the precipitation, the reaction mixture was treated with ethyl acetate (30 mL). The mixture was stirred vigorously and the precipitates were dissolved in ethyl acetate. The resultant organic layer was separated and, once again, the aqueous solution was extracted with ethyl acetate. The organic solvent was evaporated to give the solid compound. The isolated yield of precipitates in the completed reactions was in the range of 95-96%. The final product was washed several times with distillated water and recrystallized in ethanol. Obtained products were characterized by elemental analysis and spectroscopic methods.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The hydrazone Schiff base ligand, H_2L (Scheme 1), was prepared by the reaction of 3-acetylcoumarin with 2-hydroxybenzohydrazide at 1 :1 molar ratio in methanol. The elemental analysis, FT-IR and NMR spectroscopic data confirmed synthesis of the ligand. In FT-IR spectrum of H_2L (Fig. S1) the broad bands at 3400 and 3178 cm^{-1} are due to phenolic OH and amidic NH groups respectively, which the broadness indicates they are involved in the hydrogen bond interactions. The bands at 1609, 1690 and 1735 cm^{-1} are due to C=N, amidic C=O and esteric C=O functionalities, respectively [32]. ^{1}H and ^{13}C NMR spectra of the ligand (Figs. S2-S3) in DMSO-d_6 confirmed the proposed structure for H_2L. In ^{1}H NMR spectrum of H_2L the broad singlet peaks at δ 11.63 and 11.24 ppm are due to the phenolic O–H and amidic N–H groups, respectively. The peak of methyl hydrogen atoms is located at δ 2.26 ppm and the peaks at δ 6.90–7.85 ppm are due to the aromatic hydrogen atoms. In ^{13}C NMR spectrum of H_2L (Fig. S3), the peaks at δ 162.9, 159.8 and 153.9 ppm are related to amidic C=O, esteric C=O and azomethine carbon (C=N) groups, respectively, and the peak of methyl group (–CH_3) appeare at δ 16.1 ppm.

Scheme 1.

Complex **1** was synthesized through the reaction of H_2L with $ZnCl_2·4H_2O$ in methanol solution and the obtained crystalline product was then characterized by FT-IR, NMR) and single crystal X-ray studies. Comparison of the FT-IR spectra of complex with free ligand (Fig. S5) provides evidences for coordination of ligand to the Zn(II) ion in complex **1**. In the FT-IR spectrum of complex (Fig. S4) the shifts of the C=N and esteric C=O vibration bands confirms coordination of azomethine nitrogen and esteric oxygen atoms to the metal ion [28,[33]]. The bands related to NH and amidic C=O groups have been eliminated which confirm the coordination of ligand to the metal ion as mono-negative ligand in the iminol form. The broad peak at about 3400 cm^{-1} in the FT-IR spectrum of complex **1** can be attributed to the presence of OH groups involved in hydrogen bond interactions [34]. The NMR spectrum of complex **1** (Fig. S6) confirmed the coordination of ligand to the metal ion and its elemental analysis is also in agreement with the structure obtained from single crystal X-ray analysis.

The electronic spectrum of H_2L displays two absorption bands at 235 and 360 nm which based on extinction coefficients, they are assigned to intraligand $\pi \rightarrow \pi^*$ (235 nm) and $n \rightarrow \pi^*$ (360 nm) transitions. The UV-Vis spectrum of complex **1** shows three bands at 220, 310 and 410 nm which can be attributed to the intraligand and charge transfer (CT) transitions. The shifts of the absorption bands in the UV-Vis spectrum of complex relative to bands of free ligand confirm the coordination of ligand to the metal ion.

3.2. Fluorescence spectroscopy

By considering the luminescence properties of coumarins and zinc complexes, the luminescence properties of H_2L and complex **1** were investigated. The luminescence behavior of H_2L was investigated by using excitation wavelengths of 330 and 410 nm at room temperature. As shown in Fig. 1a, when the excitation wavelength was 330 nm, the maximum emission was observed for H_2L at 413 nm. Moreover, H_2L exhibited an intense fluorescent emission at 475 nm upon excitation at 410 nm. The intensity of emission at 475 nm is higher than the intensity of emission at 410 nm. These emissions can be assigned to the π–π^* transfers in the structure of H_2L [35]. The emission spectra of complex **1** by excitation wavelengths of 270, 330 and 410 nm are shown in Fig. 1b. By excitation at 270 and 330 nm, a broad emission peak was observed at about 460 nm. An intense emission was observed at 475 nm when the excitation wavelength was 410 nm. According to the previous reports [36], the photoluminescence properties of d^{10} complexes are usually due to intraligand emissions and metal-to-ligand or ligand-to-metal charge transfer (MLCT or LMCT) transitions. The luminescence mechanism in complex **1** is mainly due to the coordination of the ligand to the Zn(II) and can be attributed to intraligand emissions. The red shift in the emission spectrum of complex **1** relative to free ligand may be caused by the coordination of ligand to the metal ion.

Fig. 1.

*3.3. X-ray structure of complex **1***

The molecular structure of complex **1** determined by single crystal X-ray analysis is shown in Fig. 2. Selected bond lengths and angles around the metal ion are presented in Table 2. Diffraction studies indicated that the obtained block yellow crystals are crystallized in monoclinic system (*$P2_1/c$* space group) and they are related to a neutral mononuclear Zn(II) complex. In complex **1**, the Zn(II) ion is five coordinated, as [$ZnClO_3N$], with a nitrogen and two oxygen atoms provided by coumarin-hydrazone ligand, a chloro anion and one oxygen atom from coordinated methanol or water molecule. The coordination geometry around the Zn(II) in complex **1** can be described as distorted square pyramidal geometry with the τ value of 0.298 (where τ = the difference between the two largest angles/60; τ = 1 for ideal trigonal–bipyramidal and τ = 0 for ideal square pyramidal). Three ONO-donor atoms of the ligand and the oxygen atom of coordinated methanol/water molecule form the equatorial plane of square pyramidal geometry and the axial position is filled by chloro ligand at a distance of 2.2469(9) Å. Relative to this plane, the zinc atom is displaced toward the apical chloro ligand by 0.636 Å. The ONO-donor ligand forms a five-membered and a six membered chelate rings with the bite angles of 78.65(5)° (O3–Zn1–N1) and 83.93(4)° (O1–Zn1–N1), respectively. In complex **1** the Zn–O, Zn–Cl and Zn–N bonds are in the normal range reported for Zn(II) complexes [37].

Comparing the bond lengths of ester C=O bond in the crystal structure of complex **1** (1.2271(16) Å) with free 3-acetylcoumarin (1.207–1.211 Å) [38] indicates that it is longer in complex **1** which can be attributed to the coordination of oxygen to the metal core. This is also in agreement with the red shift of *υ*(C=O) in the FT-IR spectrum of complex **1** in comparison to the free ligand. Moreover, the N2−C12 (1.3382(17) Å) and O3−C12 (1.2742(17) Å) bond lengths in complex **1** are respectively shorter and longer than the bond length of similar group in the free hydrazone ligands (C−N ≈ 1.35 Å and C=O ≈ 1.23 Å) [39]. Moreover, the hydrogen atom of phenolic OH group is involved in intramolecular hydrogen bond interactions with the amidic nitrogen atom (N2). These observations confirm the coordination of ligand to metal ion as mononegative ligand by elimination of the amidic hydrogen atom.

There are some strong and directed intermolecular hydrogen bond interactions in the crystal structure of the complex **1** (Table 3, Fig. 3). The hydrogen atoms of the coordinated methanol or water molecules form strong hydrogen bonds with the oxygen atom of the phenolic ring. As a result, 1D polymeric chain is formed by this interaction (see Fig. 3). Moreover, the uncoordinated methanol molecule is stabilized in the crystal packing by forming O−H···O interaction with the coordinated water molecule. Also, there are strong hydrogen bond interactions between chloro ligand and hydrogen atoms from the neighboring groups (see Fig. S7).

Fig. 2.

Fig. 3.

Table 2.

Table 3.

*3.4. Thermal gravimetric analysis of complex **1***

Thermogravimetric analysis (TGA) was performed on a crystalline sample of complex **1** from ca. 30 to 800 °C at a rate of 10 °C/min under nitrogen atmosphere (see Fig. S8). The results of the thermal analysis demonstrate that the methanol and water molecules were eliminated at the first step in the range of 60-150 °C (observed 8.58%, calculated 7.92%). In the next step the chloro ligand is eliminated in the range of 250-340 °C (observed 8.34%, calculated 7.74%). Finally, the Schiff base ligand is removed in the range of 350–700 °C to give the final product which is estimated to be zinc oxide.

*3.5. Catalytic activity of complex **1** in preparing tetrazoles*

By considering the widespread applications of tetrazole derivatives in various fields [12-20], we investigated the catalytic activity of complex **1** in nitrile–azide cycloaddition reaction to produce tetrazole based compounds (see Scheme 2). For this purpose, two-component reaction between benzonitrile and sodium azide was selected as a model reaction to investigate the catalytic activity of complex **1** in preparing tetrazoles. All of the reactions were done in water as a green solvent. In the preliminary step, benzonitrile was treated with sodium azide at 90 °C in the absence of complex **1** which the results revealed that the presence of catalyst is essential for this reaction. When complex **1** (0.05 mmol) was added to the reaction flask, the reaction was started and the progress of the reaction was monitored by TLC until benzonitrile was consumed. The results of catalytic studies indicated that the reaction was completed after 7 h at 90 °C. By decreasing temperature to 70 and 50 °C, the conversion was considerably decreased in 7 h because, by TLC, considerable amount of benzonitrile was observed in the reaction mixture which indicated the reaction was not completed after 7 h. This matter indicates that temperature is one of the effective parameters in the activity of this catalytic system. The effect of the amount of catalyst was investigated by using 0.02, 0.05, 0.10 and 0.15 mmol of complex **1**. The reaction was completed in 7, 6 and 5.5 h in the case of 0.05, 0.10 and 0.15 mmol of complex **1**, respectively. By using 0.02 mmol of complex, the reaction did not finish after 12 h. These results indicate that the reaction was completed in shorter time by increasing the amount of catalyst. However, there is not a linear relationship between the amount of catalyst and the catalytic activity. By considering the results, 0.05 mmol of complex **1** was considered as the optimum amount of complex for this catalytic reaction.

Scheme 2.

To explore the potential of complex **1** in the catalytic production of tetrazoles, 4-nitrobenzonitrile, 4-methoxybenzonitrile and 4-cyanopyrdine were selected as substrates. The catalytic reactions were performed at 90 °C in the presence of 0.05 mmol of complex **1** and the summary of results is collected in Table 4. Generally, these substrates were also involved in the cyclization reaction with sodium azide in the presence of complex **1**. However, considering the results indicated that the reaction was completed in a shorter time in the case of 4-methoxybenzonitrile. On the other hand, the reaction was completed after about 9 hours in the case of 4-nitrobenzonitrile and 4-cyanopyrdine. This matter indicates that the electronic demands of the group connected to the CN moiety have considerable effect on the activity of this catalytic system. The substrate with electron donating substituent showed higher activity in comparison to the substrates containing electron withdrawing groups. Low conversion of substrates containing electron withdrawing groups can be attributed to the low coordination ability of these substrates to the metal ion which decreases the speed of the catalytic reaction.

Table 4.

In general, the complete mechanism of the reaction is not fully clear. However, on the basis of the obtained results and also by considering the reported mechanisms for the synthesis of tetrazoles [40], it is clear that the key step in this reaction is the cyclization reaction between azide and benzonitrile derivatives which are coordinated to the Zn center. A general mechanism for this catalytic reaction is shown in Scheme 3. In the first step, the azide anion can coordinate to the metal ion by elimination of a

NaCl and the benzonitrile group can coordinate to the vacant coordination site of the Zn(II) by the nitrogen atom. In this step, the cycloaddition reaction can take place between the coordinated azide and bezonitrile to the Zn(II) ion to generate the tetrazole ring. After cycloaddition, the obtained tetrazole ring is replaced by the attack of next azide ligand and the tetrazole product is released as sodium salt. The obtained Zn(II)-hydrazone-azide complex can involve in the next cycle to continue the catalytic reaction. By adding hydrochloric acid to the reaction mixture, the obtained sodium salt of tetrazole reacts with HCl to form NaCl and neutral tetrazole compound which is insoluble in the aqueous solution and precipitates in the reaction media.

Scheme 3.

Conclusion

In summary, a Zn(II) complex of coumarin-hydrazone ligand was synthesized and characterized by elemental analysis, spectroscopic methods and single crystal X-ray studies. The photoluminescent behavior of complex was also studied which revealed that complex **1** has high photoluminescent properties. The catalytic properties of the complex in cyclization reactions were investigated in preparing tetrazoles from the reaction of sodium azide and benzonitriles. The catalytic studies indicated that complex **1** is an active catalyst for green synthesis of tetrazole compounds and the electronic properties of substrate has considerable effect on the activity of this catalytic system.

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Appendix A. Supplementary material

CCDC 1864764 contains the supplementary crystallographic data for complex **1**. 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 also found, in the online version, at doi:

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Fig. 1. Emission profile of a) H_2L; b) complex **1** in methanol

Fig. 2. Molecular structure of complex **1** with atom numbering scheme. The Green dashed lines show hydrogen bond interactions.

Fig. 3. 1D polymeric chain obtained by O−H···O hydrogen bond interactions

Scheme 1. Synthesis pathway and molecular structure of H_2L

Scheme 2. Catalytic azide–nitrile cycloaddition reaction in the presence of complex **1**.

Scheme 3. Proposed general mechanism for catalytic cycloaddition reaction of azide and benzonitrile derivatives in the presence of complex **1**.

Table 1. Crystal data and structure refinement parameters for **1**

Table 2. Selected bond lengths (Å) and angles (°) for complex **1**

Table 3. Hydrogen bonding parameters (Å,°) for complex **1**

Table 4. Comparing the catalytic activity of some nitriles in cycloaddition reaction in the presence of complex **1**

Table 1. Crystal data and structure refinement parameters for **1**

	Complex **1**
net formula	$C_{18.77}H_{16.53}ClN_{25}Zn\cdot_{0.235}(CH_4O)$
M_r/g mol^{-1}	458.40
crystal size/mm	0.56 × 0.35 × 0.29
T/K	100
Radiation	Mo Kα
Diffractometer	KM4CCD
crystal system	Monoclinic
Space group	$P2_1/c$
Crystal shape, color	Block, yellow
a/Å	7.460(3)
b/Å	18.545(4)
c/Å	13.839(3)
	95.16(3)
V/Å^3	1906.8(10)
Z	4
calc. density/Mg m^{-3}	1.597
μ/mm^{-1}	1.46
F(000)	937.4
θrange	3.0–36.9
h,	−12→12
k,	−29→30
l	−23→22
R_{int}	0.054
$R(F_{obs})$	0.046
$R_w(F^2)$	0.132
S	1.00
Abs. correction	Analytical
hydrogen refinement	Mixed
measured reflections	31193
independent reflections	9032
reflections with $I > 2\sigma(I)$	7397
Parameters	286
Restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.70, -1.11

Table 2. Selected bond lengths (Å) and angles (°) for complex **1**

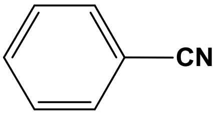
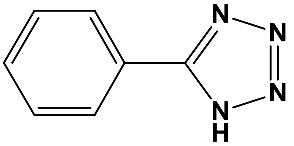
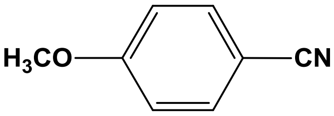
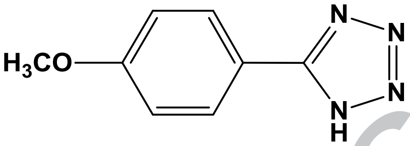
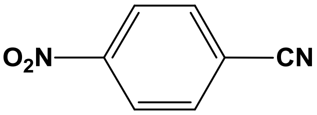
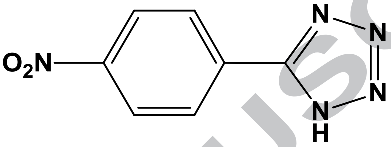
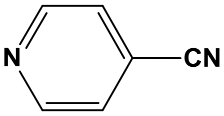
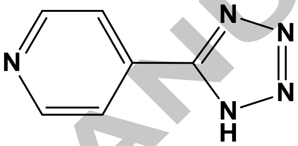
Bond	**Length/Å**	**Angles**	**deg/º**
Zn1—Cl1	2.2469(9)	O1—Zn1—Cl1	100.06(4)
Zn1—N1	2.0944(12)	O1—Zn1—N1	83.93(4)
Zn1—O1	2.0804(11)	O1—Zn1—O3	151.67(5)
Zn1—O3	2.0174(12)	O1—Zn1—O1M	84.25(16)
Zn1—O1M	2.077(5)	O3—Zn1—Cl1	107.58(4)
Zn1—O1W	1.909(18)	O3—Zn1—N1	78.65(5)
O1—C1	1.2271(16)	O3—Zn1—O1M	91.82(15)
O3—C12	1.2742(17)	O1M—Zn1—Cl1	110.21(16)
N1—C10	1.3060(17)	O1M—Zn1—N1	133.77(16)
N2—C12	1.3382(17)	N1—Zn1—Cl1	115.82(4)
N1—N2	1.3836(16)	O1W—Zn1—Cl1	104.3(6)
		O1W—Zn1—O1	85.5(6)
		O1W—Zn1—N1	139.7(6)
		O1W—Zn1—O3	93.4(6)

Table 3. Hydrogen bonding parameters (Å,°) for complex **1**

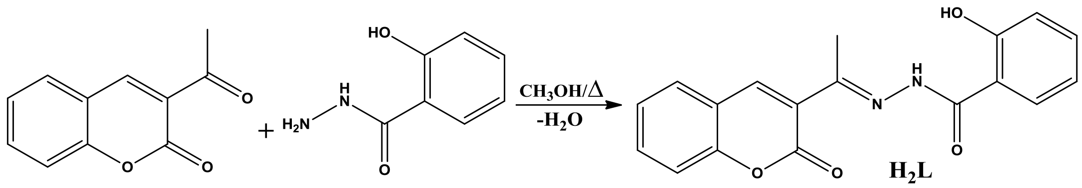
D*—*H*···*A	***D*—*H***	***H*···*A***	***D*···*A***	***D*—*H*···*A***
O4—H4···N2	0.84	1.79	2.5388 (16)	147
C17—H17···O1[i]	0.95	2.51	3.4151 (19)	160
O1*M*—H1*M*···O4[ii]	0.85	2.01	2.769 (5)	148
C1*M*—H1*MC*···O3	0.98	2.46	3.111 (3)	124
O2*M*—H2*M*···Cl1[iii]	0.84	2.24	2.997 (6)	149
O1*W*—H1*WA*···O4[ii]	0.86	2.04	2.863 (19)	160
O1*W*—H1*WB*···O2*M*	0.86	1.83	2.677 (19)	167

Symmetry codes: (i) −x+1, y−1/2, −z+3/2; (ii) −x+1, y+1/2, −z+3/2; (iii) x+1, y, z.

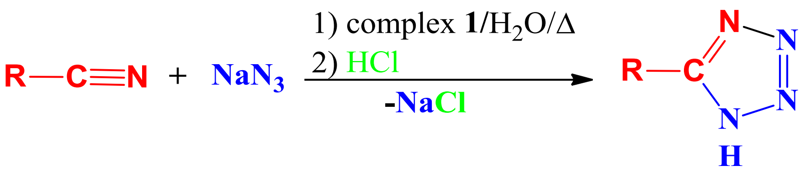
Table 4. Comparing the catalytic activity of some nitriles in cycloaddition reaction in the presence of complex **1**[a]

Entry	Substrate	Product	Time (h)
1			7
2			6.5
3			9
4			9.5

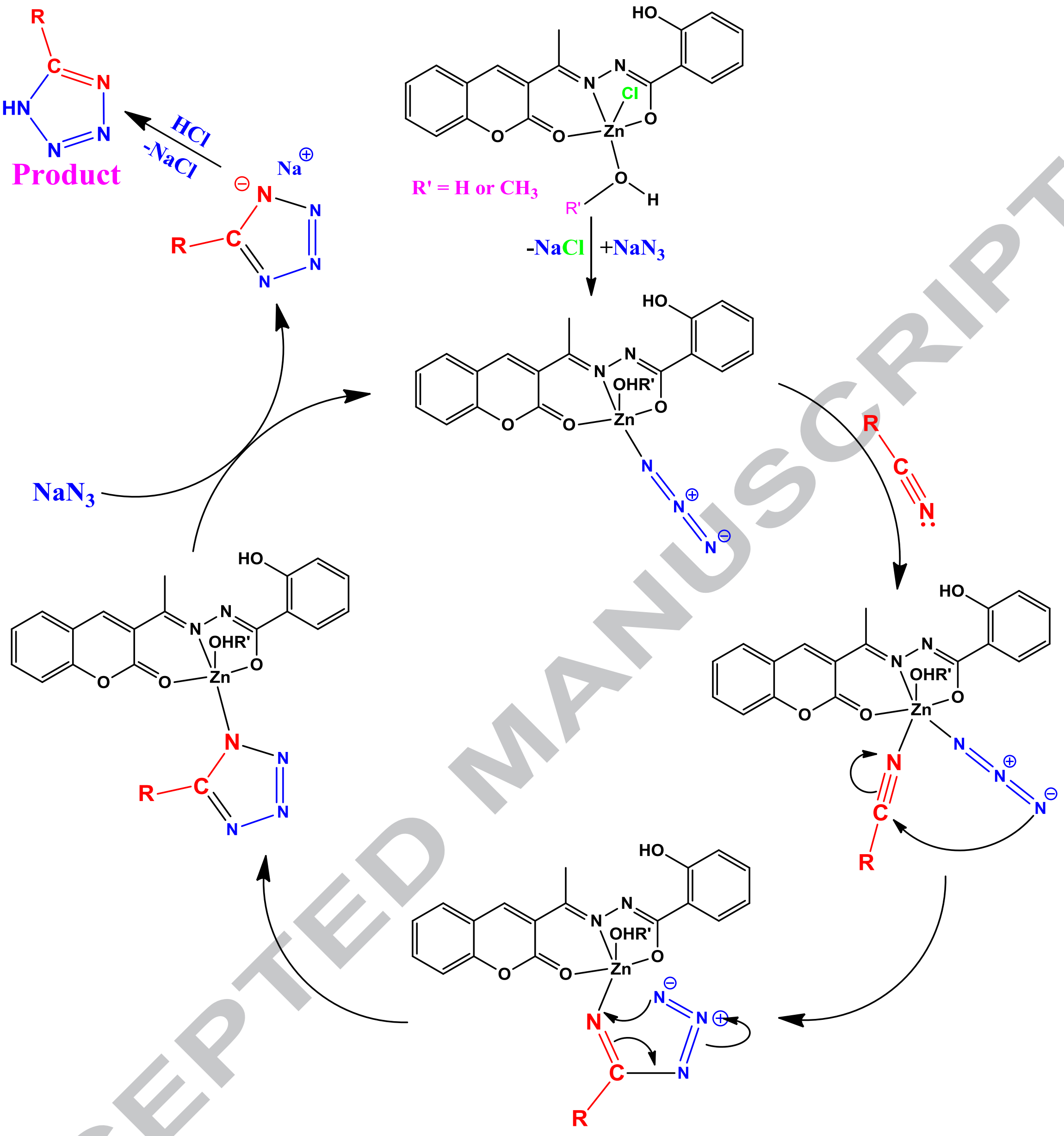
[a] *Reaction condition*: solvent = water; temperature = 90 °C; complex **1** = 0.05 mmol.



Scheme 1. Synthesis pathway and molecular structure of H_2L



Scheme 2. Catalytic azide–nitrile cycloaddition reaction in the presence of complex **1**.



Scheme 3. Proposed general mechanism for catalytic cycloaddition reaction of azide and benzonitrile derivatives in the presence of complex **1**.

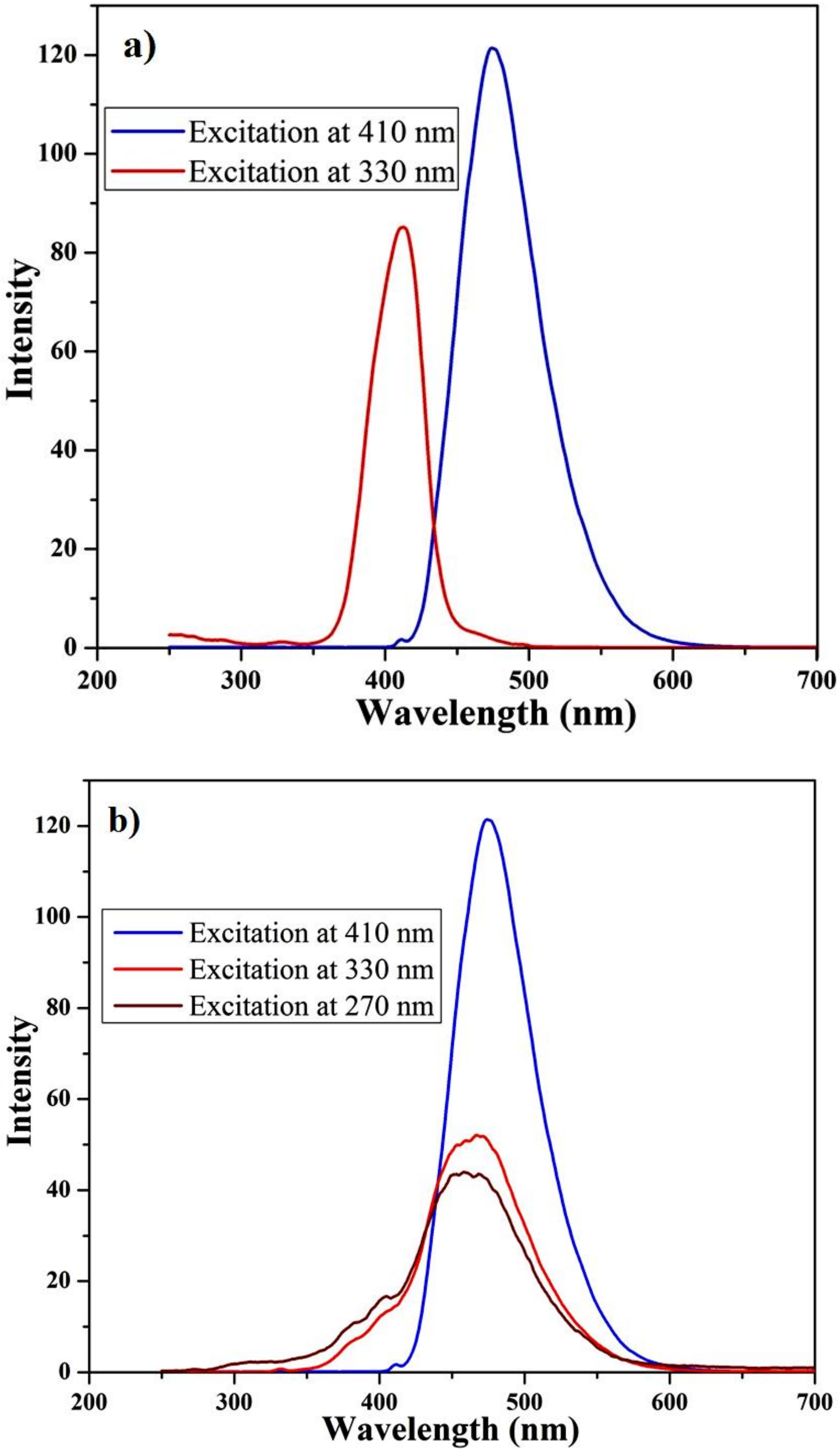


Fig. 1. Emission profile of a) H_2L; b) complex **1** in methanol

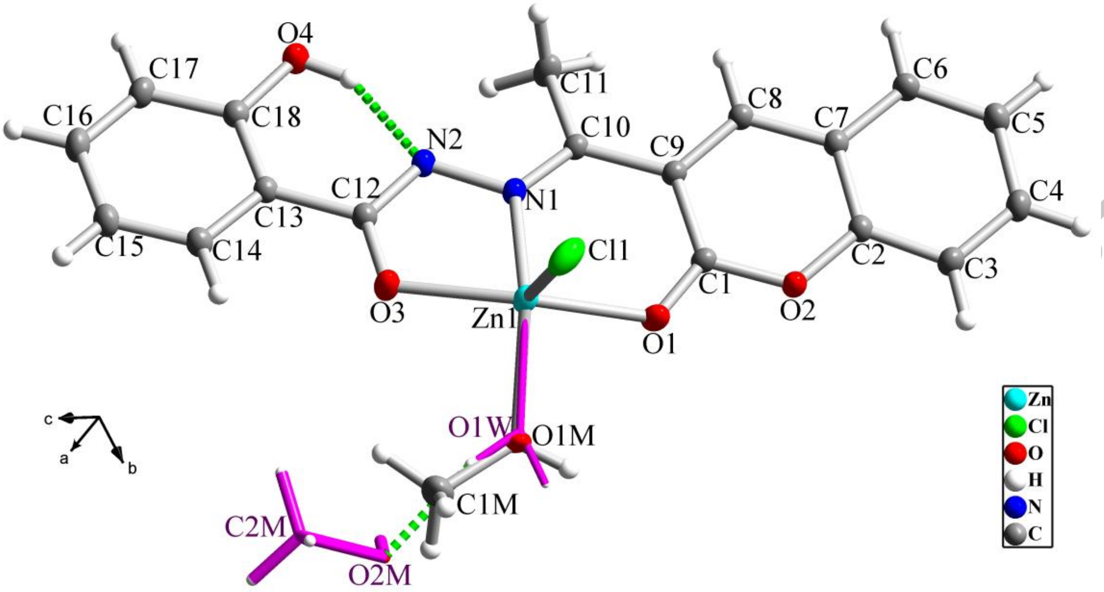


Fig. 2. Molecular structure of complex **1** with atom numbering scheme. The Green dashed lines show hydrogen bond interactions.

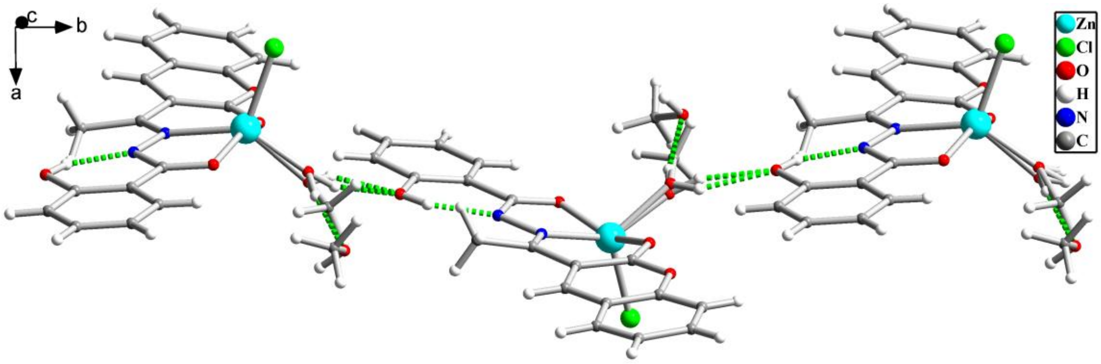
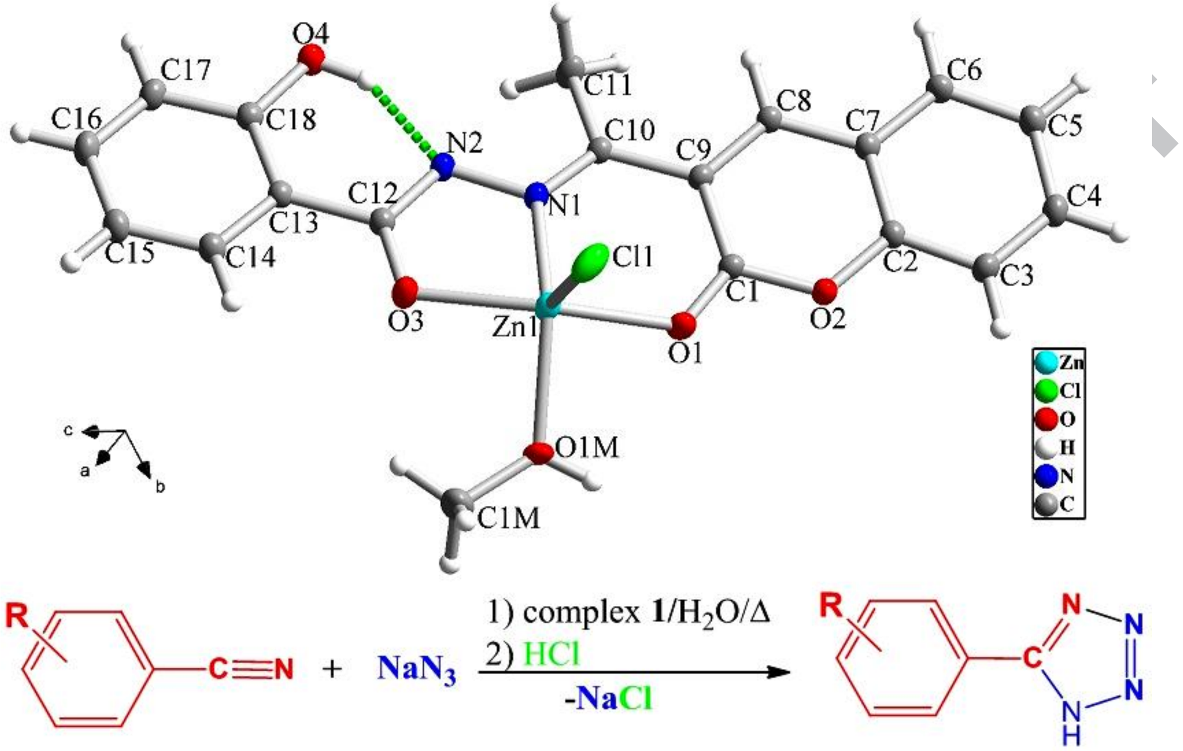


Fig. 3. 1D polymeric chain obtained by O−H···O hydrogen bond interactions

Graphical abstract



Research Highlights:

- Synthesis, characterization and crystal structure of a new Zn(II) complex with coumarin-hydrazone ligand is reported.
- Catalytic activity of Zn(II) coumarin-hydrazone complex in azide-nitrile cycloaddition reaction is investigated.
- Spectroscopic properties of Zn(II) coumarin-hydrazone complex is reported.