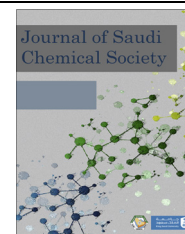




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ORIGINAL ARTICLE

Mononuclear Bis(3-aminoquinoline)Zn(II) complexes: Synthesis and structural characterization



Mohammad Azam^{a,*}, Saud. I. Al-Resayes^a, Raghavaiah Pallepogu^b,
Farha Firdaus^c, Mohammad Shakir^c

^a Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

^b Department of Chemistry, Dr. H.S. Gour University, Sagar (M.P.), India

^c Department of Chemistry, Aligarh Muslim University, Aligarh (UP), India

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KEYWORDS

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Abstract A series of two new Zn(II) complexes derived from 3-aminoquinoline are reported. The complexes were synthesized by the interaction of 3-aminoquinoline and Zn(II) ions in 2:1 molar ratio. The structure of synthesized complexes is investigated by elemental analyses, ESI-MS, FT-IR, ¹H and ¹³C NMR and UV–Vis spectroscopic studies. A single crystal X-ray diffraction measurement study reveals tetrahedral geometry around the zinc ion, and existence as a neutral discrete molecule.

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1. Introduction

Zinc is an important trace element in human beings, and is involved in several biological processes in the form of complexes with proteins and nucleic acids. Moreover, Zn(II) ions have been used in regulation of the expression of genetic information and structural maintenance of chromatin [1–4]. Studies

* Corresponding author. Tel.: +966 1 4675982; fax: +966 596441517.
E-mail address: azam_res@yahoo.com (M. Azam).

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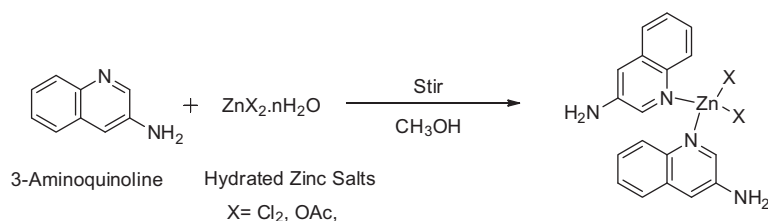
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show that any deficiency of the zinc ion can cause several neurological diseases, which can be identified by uptake, accumulation and trafficking of zinc ions [5,6]. Many zinc containing compounds have been reported to have significant antibacterial activity [7]. Various factors such as redox stability, coordination geometry and hardness of the metal ion, ligands, pH values, temperature, solvent and ligands influence the formation of zinc-containing compounds. In addition, zinc ions also play a key role in carbonic anhydrases, peptidases, proteases, and deaminases [8–13]. The heterocyclic nitrogenous compounds were first used in coordination chemistry by F. Blau in 1888 and since then, they have been extremely studied in various areas of research [14,15]. One of the heterocyclic nitrogenous compounds, quinoline, an essential part of the quinine drug, has been used to suppress

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Scheme 1 Schematic representation of synthesis of Zinc complexes.

Table 1 Crystallographic data and structure refinement for [Zn(Aqin)₂Cl₂O] complex.

Identification code	eamu104
Empirical formula	C ₁₈ H ₁₆ Cl ₂ N ₄ O _{0.5} Zn
Formula weight	432.62
Temperature/K	298
Crystal system	Triclinic
Space group	P-1
<i>a</i> /Å	8.2897(7)
<i>b</i> /Å	10.2640(8)
<i>c</i> /Å	11.4782(14)
α /°	94.512(8)
β /°	107.106(9)
γ /°	100.626(7)
Volume/Å ³	908.19(16)
<i>Z</i>	2
ρ_{calc} g/cm ³	1.582
μ /mm ⁻¹	1.658
<i>F</i> (000)	440.0
Crystal size/mm ³	0.42 × 0.32 × 0.26
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	5.92–52.736
Index ranges	–10 ≤ <i>h</i> ≤ 7, –11 ≤ <i>k</i> ≤ 12, –10 ≤ <i>l</i> ≤ 14
Reflections collected	6587
Independent reflections	3710 [<i>R</i> _{int} = 0.0345, <i>R</i> _{sigma} = 0.0616]
Data/restraints/parameters	3710/0/232
Goodness-of-fit on <i>F</i> ²	0.965
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.1045
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0675, <i>wR</i> ₂ = 0.1204
Largest diff. peak/hole/e Å ⁻³	0.41/–0.36

Table 2 Selected bond lengths and angles for [Zn(Aqin)₂Cl₂O] complex.

Zn1–C11	2.2303(9)	C8–C9	1.406(4)
Zn1–C12	2.2240(9)	C1–C2	1.389(5)
Zn1–N1	2.059(3)	C2–C3	1.372(5)
Zn1–N3	2.069(3)	C10–N3	1.328(4)
C1–N1	1.324(4)	C11–N4	1.378(4)
C2–N2	1.380(4)	C18–N3	1.375(4)
C9–N1	1.379(4)	C10–C11	1.400(5)
C12–Zn1–C11	111.01(4)	N3–C18–C13	120.4(3)
N1–Zn1–C11	111.98(8)	N3–C18–C17	119.7(3)
N1–Zn1–C12	105.95(7)	C1–N1–C9	118.2(3)
N1–Zn1–N3	106.21(11)	N1–C1–C2	124.6(3)
N3–Zn1–C11	105.02(8)	N2–C2–C1	119.5(3)
N3–Zn1–C12	116.71(8)	N1–C9–C4	120.2(3)
C1–N1–Zn1	117.9(2)	N1–C9–C8	119.4(3)
C9–N1–Zn1	123.4(2)	N3–C10–C11	124.6(3)
C10–N3–C18	118.6(3)	C10–C11–N4	119.1(3)
C10–N3–Zn1	117.1(2)	C12–C11–C10	117.4(3)
C18–N3–Zn1	124.3(2)	C12–C11–N4	123.5(3)
C3–C2–N2	122.9(4)		

Table 3 Hydrogen bonding parameters (Å, deg) of [Zn(Aqin)₂Cl₂O] complex.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	D (D...A)	\angle DHA°	Symmetry code
N2–H2A...Cl	0.88	2.79	3.4897	138	2 – <i>x</i> , 2 – <i>y</i> , 1 – <i>z</i>
N2–H2B...N4	0.88	2.57	3.4320	166	<i>x</i> , 1 + <i>y</i> , <i>z</i>
C1–H1...C12	0.95	2.78	3.4309	127	–
C7–H7...C11	0.95	2.83	3.5881	138	2 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
C10–H10...C11	0.95	2.73	3.4043	128	–

and treat malaria for the last few hundred years [16]. Recently, quinoline and its derivatives have received a lot of attention in coordination chemistry because of their coordination capability [16]. In addition, few derivatives of quinoline have also been reported in the literature as corrosion inhibitors in steel [17]. Herein, we are reporting the synthesis of Zn(II) complexes prepared by the interaction of Zn(II) ion with 3-aminoquinoline. We intended to work over 3-aminoquinoline due to its structural properties and significance in various biological and photochemical processes [16,18]. The synthesized and isolated Zn(II) complexes are characterized by spectroscopic studies along with single crystal X-ray diffraction measurements in case of complex 1.

2. Experimental

2.1. Materials and methods

3-Aminoquinoline, zinc chloride, zinc acetate and solvents were purchased from Sigma-Aldrich Co. Microanalyses (C, H and N) were carried out on Elementar Vario EL analyzer. FT-IR (4000–400 cm⁻¹) spectra were obtained on Perkin Elmer 621 spectrophotometer. ¹H and ¹³C NMR spectra of Zn(II) complexes were recorded in d₆-DMSO and CDCl₃ using JEOL-400 spectrometer. Mass spectrometry was recorded on

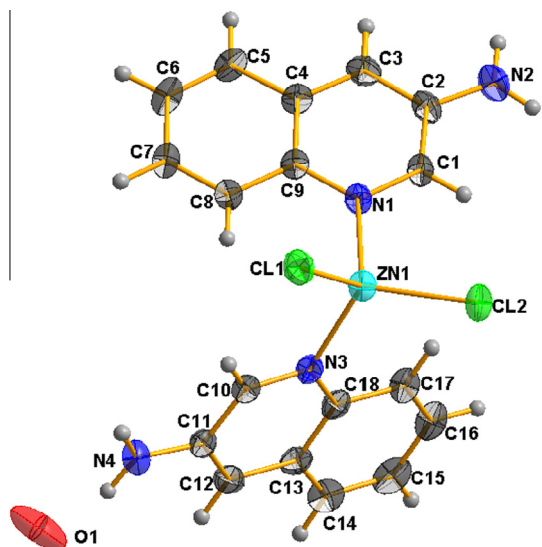


Figure 1 Crystal structure of complex 1, thermal ellipsoids are drawn at 50% probability level excepting for H atoms, which are shown as circles of arbitrary radius. The disordered water oxygen is shown with 10% probability level.

Agilent technologies ion trap LC/MS 6320 mass spectrometer with electrospray positive ionization mode. Electronic spectra of the complexes were recorded on Pharmacia LKB-Biochem, UV/Vis spectrophotometer at room temperature.

Fluorescence measurements were studied on a Shimadzu 5301 PC spectrofluorimeter equipped with a 150 W Xenon lamp and a slit width of 5 nm.

2.2. Synthesis of Bis(3-aminoquinoline)Zn(II) complexes

2.2.1. Complex 1, $[Zn(Aqin)_2Cl_2O]$

The methanol solution of $ZnCl_2 \cdot 2H_2O$ (0.8 mmol) and 3-aminoquinoline (1.6 mmol) were mixed together in 25 ml methanol in 1:2 M ratio, and stirred for 5 h resulting into a clear yellow colored solution. The colored solution was kept for evaporation at room temperature. Yellow colored crystals suitable for single crystal X-ray diffraction were isolated after a few days.

Complex 1: Yield 80%, Color: Yellow, Mp. 215 °C; Molecular formula $C_{18}H_{16}N_4ZnCl_2O$; Anal. Calc. C, 49.97; H, 3.72; N, 12.95% Found: C, 49.89; H, 3.63; N, 12.87%, FT-IR (cm^{-1} , KBr), 3440 ($-NH_2$), 1611, ($-C=N$ Aquin), 1505 ($C=C$, Aquin), 1H NMR (d_6 -DMSO): δ (ppm): 8.44 (s, 2H, $-CH=N$ -Aquin), 8.00–7.98 (d, 2H, $-CH=Aquin$, $J = 3.6$), 7.46–7.36 (m, 6H, Aquin-H), 7.16 (s, 2H, Aquin-H), 4.07 (s, 2H, $-NH_2$), 2.01 (s, 6H, $-OCO-CH_3$), ^{13}C NMR (d_6 -DMSO): δ (ppm): 143.4 (N-Aquin), 142.3 (Aquin- NH_2), $[M+H]^+$ m/z 433.58.

2.2.2. Complex 2, $[Zn(Aqin)_2(OAc)_2]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.8 mmol) in methanol was added dropwise into 3-aminoquinoline (1.6 mmol) in the same solvent (10 ml) in 1:2 M ratio. The reaction mixture

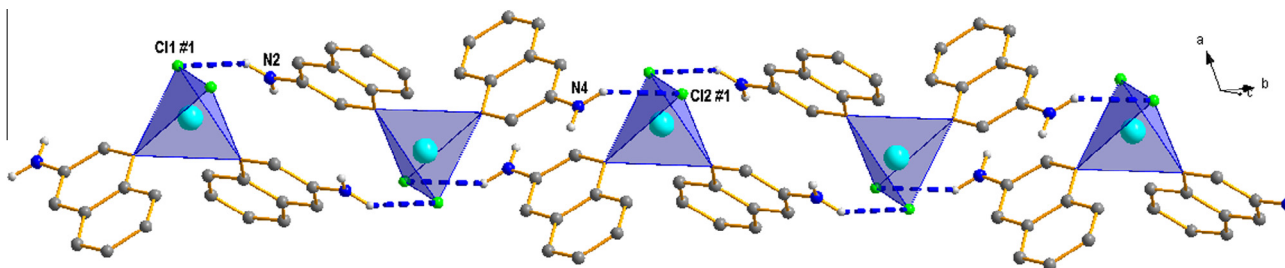


Figure 2a One dimensional chain formed by N-H...Cl hydrogen bonds.

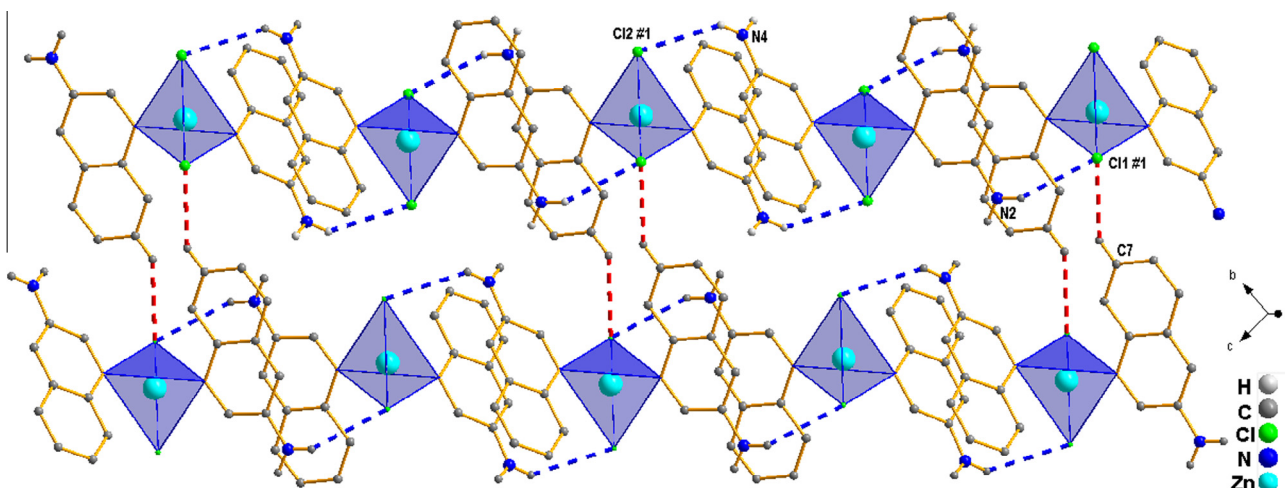


Figure 2b 2 D sheet like supramolecular structure formed by N-H...Cl hydrogen bonds and π - π stacking interactions.

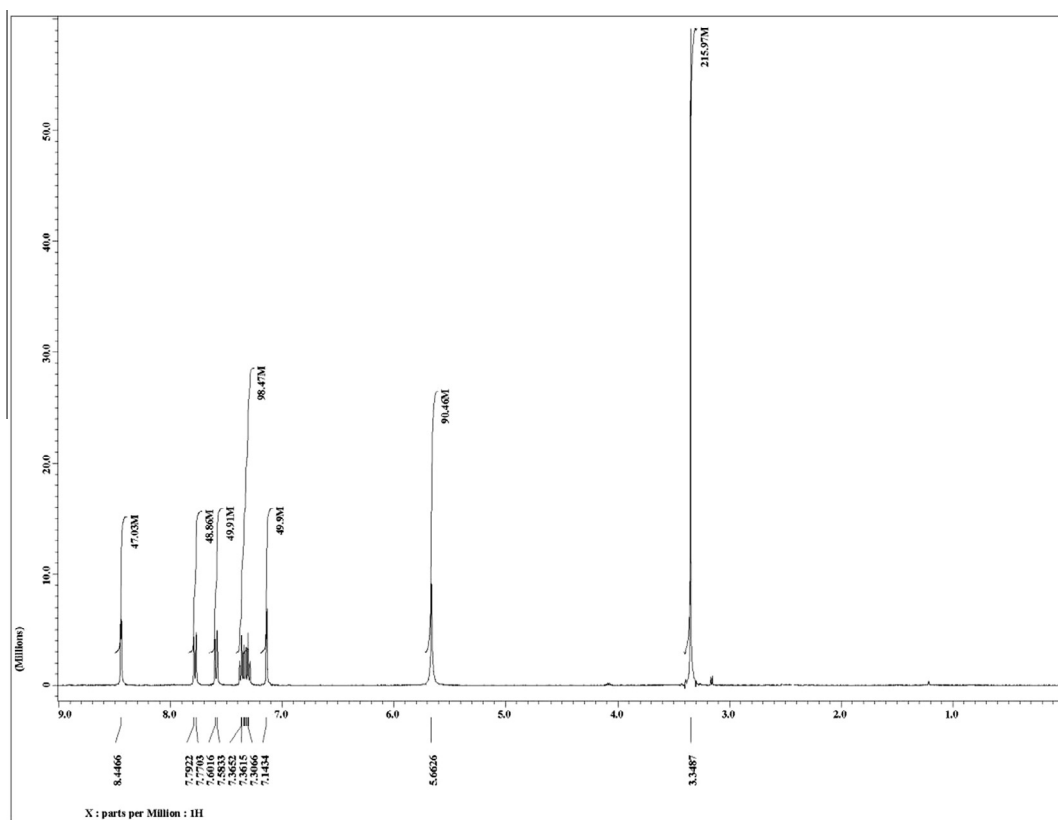


Figure 3 ^1H NMR spectrum of complex 1.

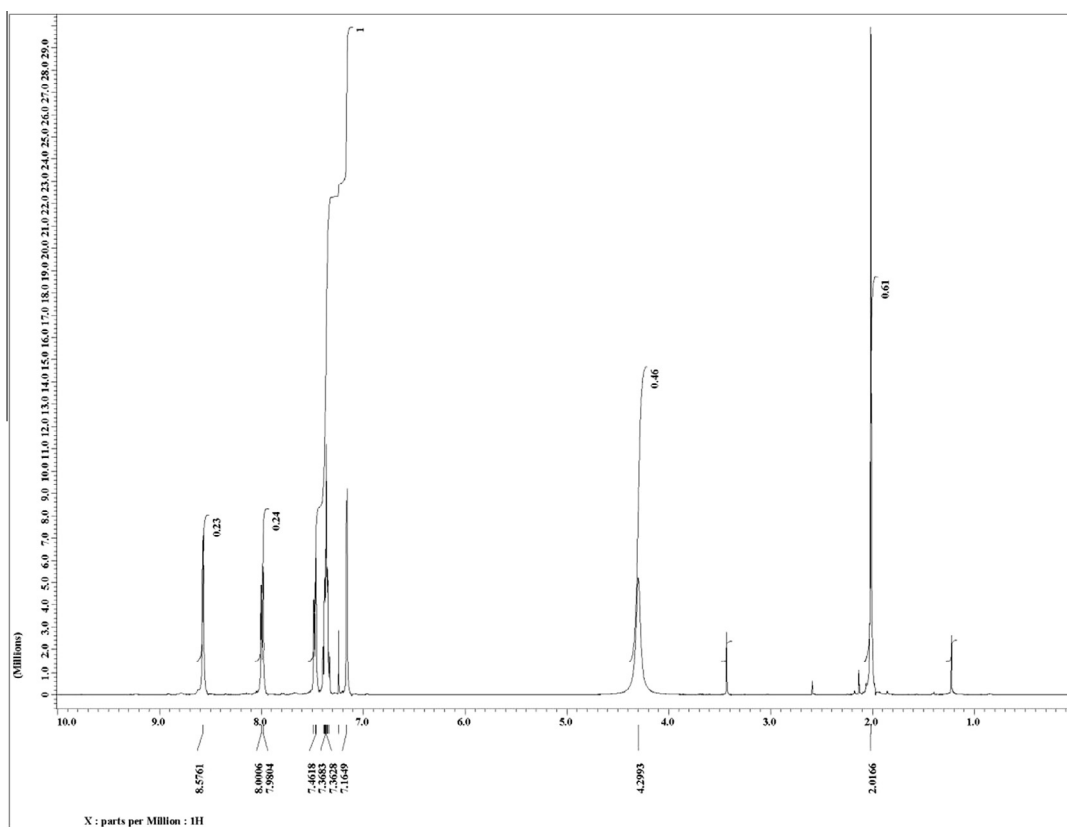


Figure 4 ^1H NMR spectrum of complex 2.

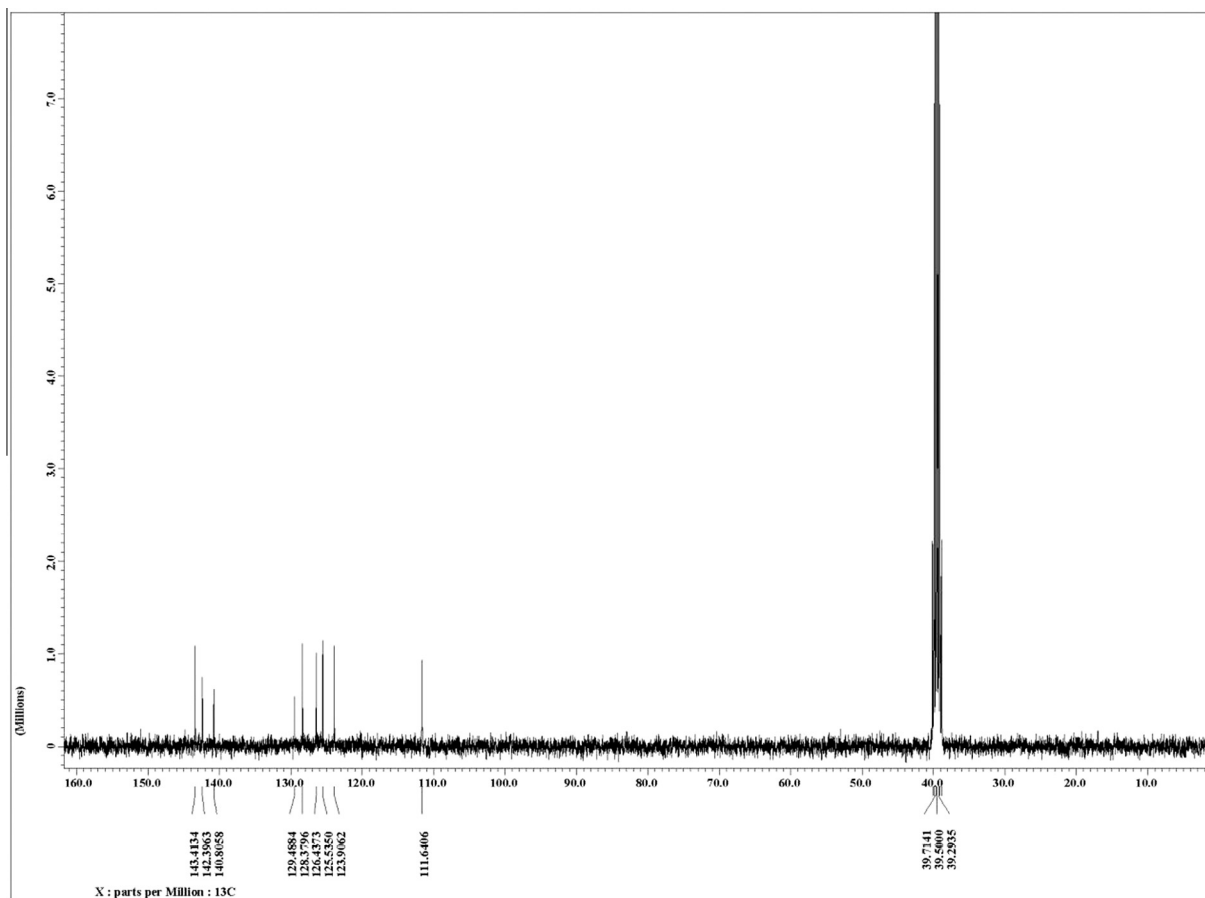


Figure 5 ^{13}C NMR of complex 1.

was stirred for 3 h. Slight turbidity appears which is removed by filtration, and the filtrate is kept for crystallization at room temperature. After a few days, yellow colored microcrystalline product obtained was isolated. Unfortunately we couldn't find any crystal suitable for X-ray diffraction measurements.

[Zn(Aquin) $_2$ (OAc) $_2$] Complex: Yield 75%, Color: White, Mp. 190 °C; Molecular formula $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_4\text{Zn}$; Anal Calc. C, 56.00; H, 4.70; N, 11.87% Found: C, 55.84; H, 4.68; N, 11.84%, FT-IR (cm^{-1} , KBr), 3324 ($-\text{NH}_2$), 1608 ($-\text{C}=\text{N}$, Aquin), 1499 ($\text{C}=\text{C}$, Aquin), ^1H NMR (CDCl_3): δ (ppm): 8.57 (s, 2H, $-\text{CH}=\text{N}$ -Aquin), 8.00–7.98 (d, 2H, $-\text{CH}=\text{Aquin}$, $J = 3.6$), 7.46–7.36 (m, 6H, Aquin-H), 7.16 (s, 2H, Aquin-H), 4.07 (s, 2H, $-\text{NH}_2$), 2.01 (s, 6H, $-\text{OCO}-\text{CH}_3$), ^{13}C NMR (d_6 -DMSO): δ (ppm): 143.4 (N-Aquin), 141.2 (Aquin- NH_2), 22.8 ($-\text{CH}_3$), 180.2 ($\text{O}-\text{CO}$), $[\text{M} + \text{H}]^+ m/z$ 472.75.

2.2.3. Single crystal X-ray structure of complex 1

The crystal data for complex 1 were collected on an Oxford X-calibur Gemini diffractometer equipped with EOS CCD detector using monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The structure refinements were made against F^2 using SHELXL-97 [19]. The oxygen atom of the water molecule (half water) present in the crystal structure of complex 1 was disordered, and occupied a special position.

3. Results and discussion

Reaction of 3-aminoquinoline with Zn(II) ions in methanol yields mononuclear complexes with high yields (Scheme 1). The isolated complexes are soluble in common organic solvents. The synthesis of isolated complexes was confirmed by the findings obtained from elemental analyses, ESI-MS, UV/Vis, FT-IR and ^1H and ^{13}C NMR spectroscopy. Structure of complex 1 was also confirmed by single crystal X-ray diffraction measurement, which shows that the complex maintains a tetrahedral geometry.

Crystallographic data and refinement details for the structural analyses of the complex 1 are summarized in Table 1. Selected bond lengths and bond angles are presented in Table 2 while selected parameters for weak interactions are listed in Table 3. Thermal ellipsoidal plots of the complex are shown in Fig. 1. The single crystal X-ray structure determination reveals that the complex crystallizes in triclinic centrosymmetric P-1 space group, and all atoms are situated in general positions except water oxygen which is located on a special position, thus making the whole complex a neutral discrete molecule. Each asymmetric unit consists of a Zn(II) complex and half water molecule and there are two such units in the unit cell. In the crystal structure, each Zn(II) ion is bonded to two 3-aminoquinoline rings via quinolone nitrogen, and two chloride ions in a tetrahedral fashion (Fig. 1). Interestingly, each Zn(II) ion is connected through $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen

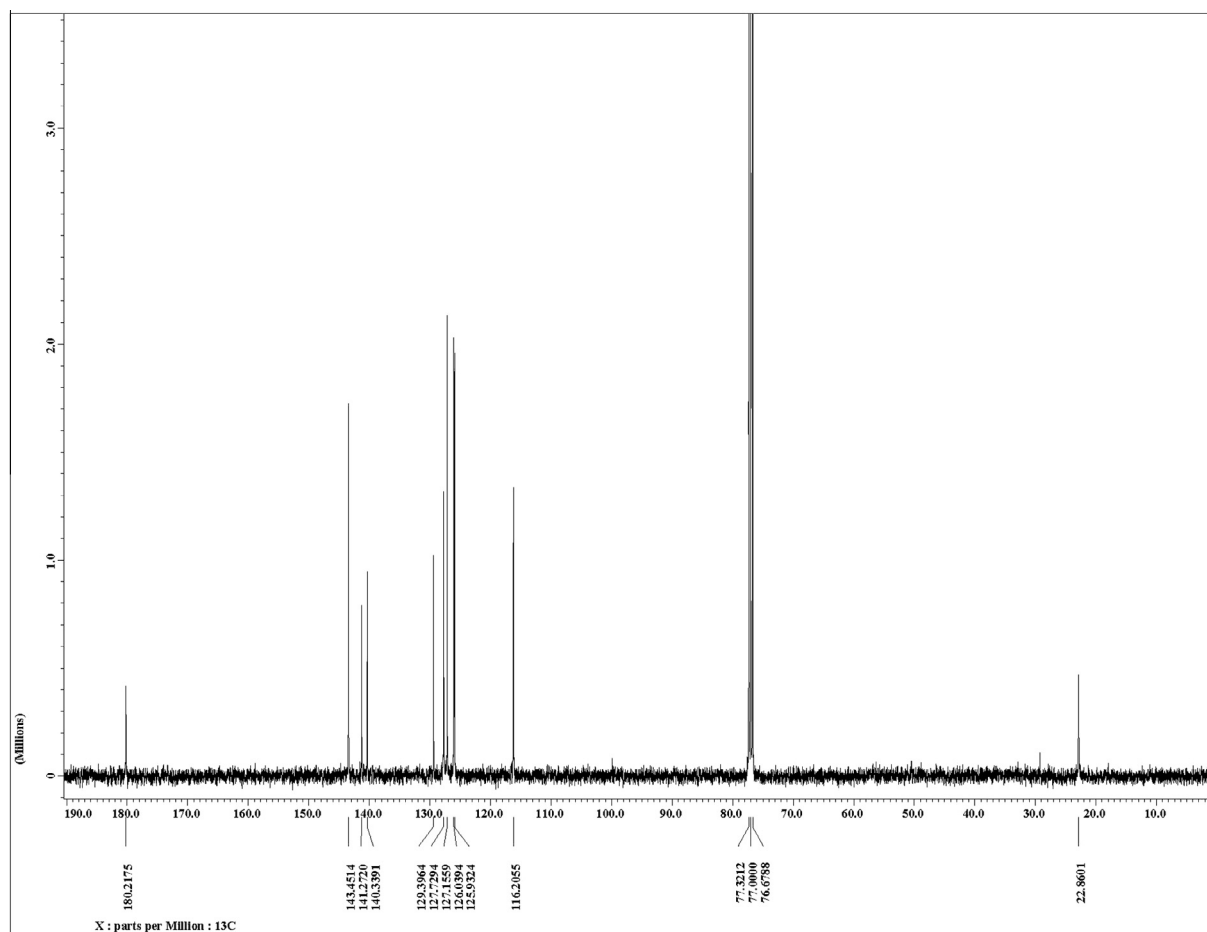


Figure 6 ^{13}C NMR of complex 2.

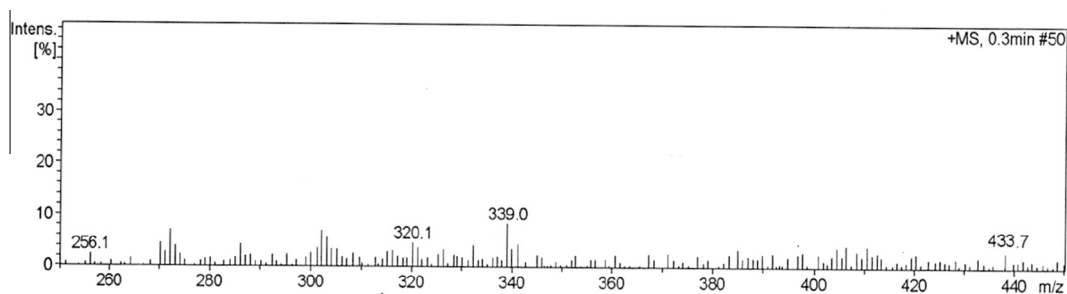


Figure 7 ESI-MS spectrum of complex 1.

bonds in *b* axis in a head to tail fashion. Two independent chains are linked through $\text{C-H}\cdots\text{Cl}$ hydrogen bonds formed between hydrogen of C7 carbon of 3-aminoquinoline and chloride ion of a parallel chain, in addition to π - π stacking interactions between two 3-aminoquinoline rings at a distance of 3.53 Å. It results in the formation of a 2D sheet-like supramolecular structure (Fig. 2a and 2b). There was no significant difference in IR spectra of both the complexes (Fig. 1S). The presence of bands at 3400 cm^{-1} were assigned to a stretching vibration of a non-coordinated $-\text{NH}_2$ group, and appeared at a lower wave number than their parent ligand [20]. The absorption bands at 1608 – 1611 cm^{-1} and 1499 – 1505 cm^{-1} were assigned to $\text{C}=\text{N}$ and $\text{C}=\text{C}$ of aromatic ring vibrations, respectively, while the rest of the bands were

found at their expected positions [21,22]. The peaks at 1624 cm^{-1} and 1432 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of coordinated acetate group in complex 2 [23]. The ^1H NMR spectra of Zn(II) complexes show resemblance with that of free aminoquinoline ligand (Fig. 2S), and shows appreciable shifts in all aromatic protons including amino protons, thus suggesting the coordination of 3-aminoquinoline to Zn(II) ion. The ^1H NMR spectra of complex 2 resemble those of complex 1. However, $-\text{NH}_2$ protons are observed at 4.07 ppm in both the complexes. Singlet for $-\text{CH}=\text{N}$ proton (s, 2H, $-\text{CH}=\text{N}$ -Aquin) appears at 8.44 ppm and 8.67 ppm (s, 2H, $-\text{CH}=\text{N}$ -Aquin) for complex 1 and 2, respectively. The aromatic protons for the aminoquinoline ring were found at 7.16–8.00 ppm

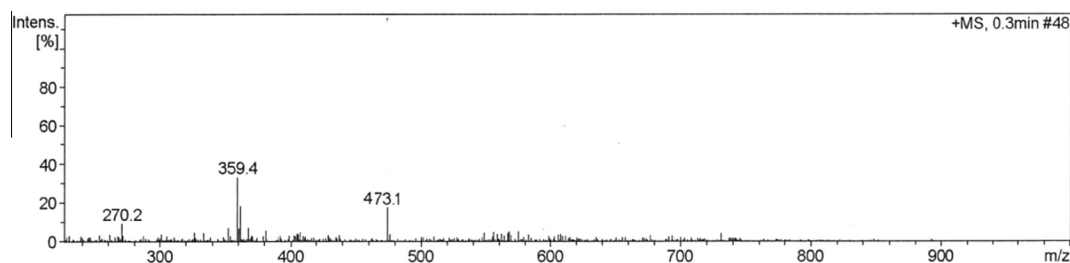


Figure 8 ESI-MS Spectrum of complex 2.

(m, 10H, Aminoquin-H) in both the complexes. However, one additional singlet for the methyl proton of the acetate group was observed at 2.01 ppm (s, 6H, $-\text{OCO}-\text{CH}_3$) in complex 2 (Figs. 3 and 4). Furthermore, structure of the synthesized complexes was again confirmed by ^{13}C NMR spectral data which support ^1H NMR spectral findings. Both the complexes have almost similar ^{13}C NMR spectra. But complex 2 shows two additional peaks for $-\text{OCO}-$ and $-\text{CH}_3$ carbons (Figs. 5 and 6). A signal appearing at 142.3 ppm and 141.2 ppm may be assigned to the carbon belonging to Aquin- NH_2 in complexes 1 and 2, respectively, while the rest of the signals were found at their expected positions. ESI mass spectra also confirmed the synthesis of complexes and showed molecular ion peaks, $[\text{M} + \text{H}]^+$ at 433.58, 472.75 corresponding to their molecular formulae, $[\text{C}_{18}\text{H}_{16}\text{N}_4\text{ZnCl}_2\text{O}]$ and $[\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_4\text{Zn}]$, respectively (Figs. 7 and 8).

The UV/Vis spectra of both the complexes recorded in methanol at concentration 0.25×10^{-5} M showed three prominent absorption bands at ca. 245 nm, 301 nm, which are due to intra-ligand charge transitions (Fig. 4S). [24–26], A weak transition at ca. 401 nm is assigned to MLCT [20,24–26]. Dissolution of complexes 1 and 2 in methanol reported at room temperature showed significant fluorescent intensities. Complexes 1 and 2, upon excitation at 245 nm and 301 nm, have fluorescence emission bands at 310 nm and 362 nm, respectively [27]. Thus, the fluorescence emission observed in the complexes may be due to metal-to-ligand charge, and red shift reported for both the complexes is above 50 nm [28–31].

Acknowledgements

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Appendix A. Supplementary data

CCDC 1033787 contain the supplementary crystallographic data for $[\text{Zn}(\text{Aquin})_2\text{Cl}_2\text{O}]$, which 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 <http://dx.doi.org/10.1016/j.jscs.2015.11.005>.

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