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La(III) complex involving the O,N-donor environment of quinazoline-4(3H)-one Schiff's base and their antimicrobial attributes against methicillin-resistant *Staphylococcus aureus* (MRSA)

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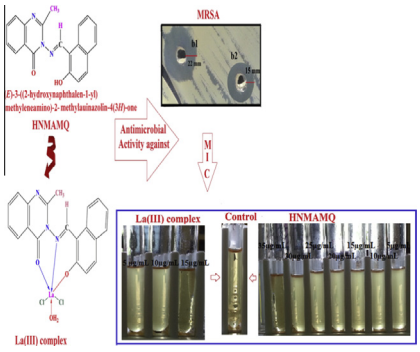
HIGHLIGHTS

- Synthesis and characterization of new quinazoline-4(3H)-one Schiff's base and its La(III) complex.
- Methicillin-resistant *Staphylococcus aureus* were isolated from Gulbarga region, India.
- La(III) complex shows enhanced antimicrobial activity over Schiff's base.

GRAPHICAL ABSTRACT



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ABSTRACT

The incidence of methicillin-resistant *Staphylococcus aureus* increased during the past few decades, so there is an urgent need of new antimicrobial agents if public health is concerned. Though the Schiff's bases and La(III) complex have enormous biological activity, but less attention was given in their synthesis. In the present investigation, we synthesized a new (E)-3-((2-hydroxynaphthalen-1-yl) methyleneamino)-2-methylquinazoline-4(3H)-one HNMAMQ Schiff's base by the condensation of 3-(2-aminophenyl) quinazolin-2-methyl-4(3H)-one and 2-hydroxy-1-naphthaldehyde. The Schiff's base HNMAMQ and its La(III) complex were characterized by elemental analyses, IR, NMR, mass spectra, and thermal studies. The newly synthesized Schiff's base HNMAMQ and its La(III) complex were evaluated for their antimicrobial activity against methicillin-resistant *Staphylococcus aureus* isolated from the Gulbarga region in India. The Schiff's base HNMAMQ and its La(III) complex showed good antimicrobial activity and thus represents a potential new drug of choice.

Introduction

Staphylococcus aureus (*S. aureus*) resistant to methicillin is a major problem that the world is now facing. The antibiotic era, barely 60 years old, is also threatened because of increase resistance rhythm of this organism against different antibiotics [1]. Today's challenging task is to synthesize a new antimicrobial agent that does not generate microbial resistant so, studies in finding out new antimicrobial agents against methicillin-resistant *Staphylococcus aureus* (MRSA) are desperately required if public health crisis is to be averted. MRSA were isolated at low levels, a decade ago, but is currently widespread [2] due to the development of resistant to methicillin antibiotic which exponentially increased high

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morbidity and mortality [1,3] so there is an urgent need of a new antimicrobial agent who does not generate resistance against MRSA.

Alternate to antibiotics are the Schiff's base and its metal complexes [4] at present, playing a key role in the development of coordination chemistry, especially the quinazoline-4(3H)-one [5,6] having vast applications in the field of medical microbiology such as anti-cancer and anti-viral activities. Further, its metal complexes have been widely studied because of their anti-fungal, antibacterial, anti-tubercular activities, herbicidal applications, and cheating abilities which attracted remarkable attention [7].

Recently, there has been growing interest in the lanthanide-Schiff's base complexes owing to the important applications of both metals and ligands [8]. Lanthanides are the rare earth complexes [9] discovered in the 19th century and form the longest series of the periodic table. They are the best ions form, highly stable complexes because of their nature with a high coordination number [10]. Initially coordination chemistry of lanthanides was limited as a strongly chelating ligands but, with the development of new complex forming compounds, a significant number of lanthanide complexes with various types of ligands were synthesized and characterized [11] and showed a wide variety of medicinal and biochemical applications. In particular, they are used as a diagnostic tool in biomedical analysis as MRI contrast agents [12,13], in Fluoro-immuno assays [14], as an anti-cancer, and antimicrobial agent [15].

In the light of above vast applications of lanthanide complexes, their scanty reports when compared to d-block transition metal complexes [16] and in continuity our work on chemistry of quinazoline-4(3H)-one Schiff's base and its metal complexes [17] in the present study, we made an attempt to solve challenging task, "methicillin drug resistant problem" in this regard, we synthesized a new lanthanide [La(III)] complex derived from (E)-3-((2-hydroxynaphthalen-1-yl) methyleneamino)-2-methylquinazoline-4(3H)-one HNMAMQ and assayed their antimicrobial activity against MRSA isolates collected from various hospitals and health care centers in the Gulbazzrga region.

Materials and methods

Blood agar, Mannitol salt agar, Mueller Hinton agar (MHA) and Mueller Hinton Broth (MHB) were procured from Hi-media. Elemental analysis (C, H and N) were carried out using micro analytically Perkin Elmer 240C Instrument. IR spectra of the Schiff's base HNMAMQ and its La(III) complex in KBr pellets were recorded on Perkin Elmer Spectrum one FT-IR spectrometer in the spectral range 4000–350 cm^{-1}. The ^1H NMR spectra were recorded on AMX-400 NMR spectrometer, using Tetramethylsilane [TMS] as an internal standard and dimethyl sulphoxide [DMSO] as a solvent. Mass spectra were recorded with a JEOL GCMATE II GC–MS mass spectrometer. Magnetic susceptibilities were measured on a Gouy balance at room temperature using $Hg[Co(NCS)_4]$ as calibrant. Thermal analyses were measured from room temperature to 1000 °C in N_2 on a Perkin Elmer, Diamond TG/DTA model thermal analyzer with a heating rate of 10 °C min^{-1}. The molar conductance data were recorded on the ELICO-CM-82T conductivity bridge in DMF solution at concentration $\sim 10^{-3}$ M.

Chemistry of Schiff's base HNMAMQ and its La(III) complex synthesis

Easy and efficient strategy was undertaken to synthesize the target quinazoline Schiff's base which involves the following three steps. In the first synthesis step, a warm solution of methyl anthranilate reacts with acetic anhydride in 20 mL methanol, results in the formation of a cyclic compound 2-methyl-4H-benzo [d] [1,3] oxazin-4-one. The second step involves the reaction between 2-methyl-4H-benzo [d] [1,3] oxazin-4-one and hydrazine hydrate in 20 mL hot methanol to afford 3-amino-2-methylquinazoline-4(3H)-one [18]. Finally, in the third step the simple condensation reaction between 3-amino-2-methyl quinazoline-4-one and 2-hydroxy-1-naphthaldehyde results in the formation of the Schiff's base (E)-3-((2-hydroxynaphthalen-1-yl) methyleneamino)-2-methylquinazoline-4(3H)-one HNMAMQ as presented in supplementary file Fig. S1. The progress of the reaction was continuously monitored by the aid of thin layer chromatography (TLC) on a silica gel-G coated aluminum plates (Merck) and spots were visualized by exposing the dry plates to iodine vapors.

Chemistry of HNMAMQ

Obtained as yellowish green solid has a Molecular formula $C_{20}H_{15}N_3O_2$, Yield 85%, mp. 270 °C. Anal. (%): Calcd. C, 72.94; H, 4.59; N, 12.76. Found: C, 72.24; H, 4.12; N, 11.97. IR (KBr, cm^{-1}): 3385 ν(OH), 1580; ν(>C=N), 1690; ν(>C=O). ^1H NMR (DMSO-d_6, δ ppm): 10.61, (s, 1H, OH); 8.35, (s, 1H, >C=N); 2.41–2.43, (s, 3H, CH_3); 6.82–8.54, (m, 10H, Ar—H). MS *m*/*z*: 329 [M^+].

Synthesis of La(III) complex

The method used for the synthesis of metal complex involves the interaction of metal salt with ligand in a molar ratio (M:L = 1:1). A hot methanolic solution (30 mL) of the Schiff's base HNMAMQ was added to a stirred solution of La(III) chloride in methanol (20 mL) having a required molar ratio of M:L (1:1). The mixture was refluxed for about 3 h at a temperature of ~78 °C. Subsequently, sodium acetate was added to adjust the pH 6.0–7.0. The solid, intense colored complex formed was immediately precipitated out. The precipitated complex was further refluxed for about 1 h to check its stability. Later it was filtered off, washed thoroughly with water along with little warm methanol for apparent dryness and finally dried in a vacuum over fused $CaCl_2$.

The chemistry of La(III) complex

Obtained as white solid has a Molecular formula $[La(C_{20}H_{14}N_3O_2)Cl_2H_2O]$ Yield 78%, mp. 296 °C. Anal. (%): Calcd. C, 43.19, H, 2.90, N, 7.56, M, 24.98, Cl, 12.75. Found: C, 43.08, H, 2.52, N, 7.28, M, 24.74, Cl, 12.54. IR (KBr, cm^{-1}): 1566, ν(>C=N); 1675, ν(>C=O), 3395 (H_2O). ^1H NMR (DMSO-d_6, δ ppm): 8.42, (s, 1H, >C=N); 2.64–2.67, (s, 3H, CH_3); 2.71 (s, 1H, H_2O), 6.97–8.72 (m, 10H, Ar—H). MS *m*/*z*: 556 [M^+], 558 [M + 2] and 560 [M + 4].

Isolation and identification of MRSA

Samples like blood, pus and other exudates were obtained from different hospitals and health care centers of the Gulbarga region in India. Initially, all the samples were first inoculated onto blood agar plates. The plates were incubated at 37 °C for 24–48 h. Further, the colonies obtained on blood agar after incubation was again inoculated onto mannitol salt agar; the plates were once again incubated at 37 °C for 24–48 h. The preliminary identification of *S. aureus* were detected by change in color of the medium from red to yellow due to mannitol fermentation. Further, the *S. aureus* were identified based on morphological, microscopic and biochemical tests [1] among the identified *S. aureus,* MRSA were detected phenotypically by means of antibiotic susceptibility test as per the guidelines recommended by the Clinical and Laboratory Standards Institute (CLSI-2012) [19].

Antimicrobial activity against MRSA

The antibacterial activities of newly synthesized Schiff's base HNMAMQ and its La(III) complex against MRSA were evaluated

on MHA by making a lawn of MRSA (0.5 McFarland) with the aid of sterile cotton swabs, wells of 6 mm diameter were punched carefully with the help of a cork borer. Further, the wells were loaded with 150 μg/mL (in DMSO as a solvent) of different investigated test compounds. The plates were incubated at 37 °C for 24 h. Antibacterial activity was determined by measuring the zone of inhibition.

Determination of minimum inhibitory concentration (MIC)

The MIC is defined as the lowest concentration of an antimicrobial agent that will inhibit the visible growth of microorganisms. To determine MIC different volumes of investigating test compounds (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 μg/mL) and MRSA culture (0.5 McFarland) was added into MHB and were incubated at 37 °C for 18 h. The last tube with no growth of microorganism was recorded to represent the MIC. The antibacterial activities of test compounds were compared with standard methicillin antibiotic.

Results and discussion

Based upon the analytical and physical data it was clearly revealed that, all the synthesized compounds were very stable for a long period of time and non hygroscopic in nature at room temperature. The complex was sparingly soluble in common organic solvents, however completely soluble in DMF and DMSO.

The synthesized compounds were characterizations via their physical, analytical, and spectral data. The stoichiometry reaction between the La(III) ion and the Schiff's base HNMAMQ in a molar ratio of M:L (1:1) resulted in the formation of the metal complex of type ML [where M = La(III)] exhibiting octahedral geometry through the involvement of azomethine nitrogen and carboxylic oxygen with metal ion as shown in Fig. 1. The observed molar conductance values were in the range of 55–57 Ohm^{-1} cm^2 mol^{-1} in DMF, indicates the electrolytic nature of metal complex [20]. The metal and chloride contents were determined as per standard procedure [21]. The magnetic moment of the La(III) complex was consistent with the presence of unpaired 4f electrons and close to the values for the free metal ions as reported by Van Vleck and Frank [22]. These observations suggest that the 4f electrons of the La(III) do not take part in bond formation in these species suggesting its diamagnetic nature.

The elemental analysis (C, H, and N) data of the Schiff's base HNMAMQ and its La(III) complex were in good agreement with proposed molecular formula.

The infra red spectrum of the Schiff's base HNMAMQ displays a broad band in the region of 3385 cm^{-1} owing to ν(—OH) of naphthalene moiety. The absence of this band upon complexation, in other words proton substitution by cation coordination to the oxygen atom of the Schiff's base HNMAMQ reveals the participation of phenolic oxygen in bonding with La(III) ion via deprotonation [23]. The ^{1}H NMR spectrum of the La(III) complex shows the disappearance of —OH proton signal at δ 10.61 ppm (s, 1H) (D_2O exchangeable) of the Schiff's base HNMAMQ upon complex formation, further support the participation of phenolic oxygen in coordination via deprotonation. In the IR spectrum of the Schiff's base HNMAMQ a characteristic high intense band was appeared in the region of 1598–1592 cm^{-1} due to azomethine ν(>C=N), which experiences a negative shift of 15–20 cm^{-1} in La(III) complex, mainly due to the drift of the lone pair density of azomethine nitrogen towards the metal ions, indicates coordination of azomethine nitrogen with the metal ions [24]. Further, this was confirmed by ^{1}H NMR spectra, owing to the downfield shift of the azomethine proton signal from δ 8.35 ppm (s, 1H, >CH=N) of the Schiff's base HNMAMQ to δ 8.42 ppm (s, 1H, >CH=N) in La(III) complex, shows the involvement of >CH=N nitrogen in coordination. In the IR spectrum of the Schiff's base HNMAMQ, a high intense, strong band in the region of 1720–1715 cm^{-1} was assigned to the carboxyl group of quinazoline ring (>C=O). However, upon complex formation shows a downfield shift of 20–30 cm^{-1} indicates the participation of carboxylic oxygen [25]. The low frequency skeletal vibrations bands in La(III) complex assigned to ν(M—O) and ν(M—N) were appeared in the region of 557–550 cm^{-1} and 452–445 cm^{-1} respectively, which further support the coordination of the Schiff's base HNMAMQ through the nitrogen of azomethine, carboxylic and phenolic oxygen with La(III) ion [26]. The ν(M—N) band was usually sharp and strong while, the ν(M—O) band was broad, since a large dipole moment change was involved in the vibrations of the M—O bond comparison to that of the M—N bond. Hence it was expected that the ν(M—O) band should appear at a higher energy in compared to that of the ν(M—N) band [27]. The M—O bond length was shorter than the M—N bond length and this also supports the occurrence of the ν(M—O) band at a higher energy in comparison to that of the ν(M—N) band. Moreover, a weak band was observed in the range of 355–350 cm^{-1} assigned to ν(M—Cl), characteristic of the chloride atom in La(III) complex and was further confirmed by quantitative chloride estimation. In comparison with Schiff's base HNMAMQ, the La(III) complex shows the appearance of broad band around 3405–3395 cm^{-1} attributed to the ν(OH) stretching frequencies shows the existence of coordinated water molecules and the appearance of characteristic rocking frequency at 810 cm^{-1} [28] which was further confirmed through thermal analysis study. The remaining signals were appeared in their expected regions. A new characteristic singlet proton signal at δ 2.72 ppm owing to the presence of a coordinated water molecule was obtained. Hence, from the above observations, it was evidently concluded that the total number of protons calculated from the integration curves and the values obtained from their C, H, and N analysis is in agreement with each other thereby reflecting the purity of compounds.

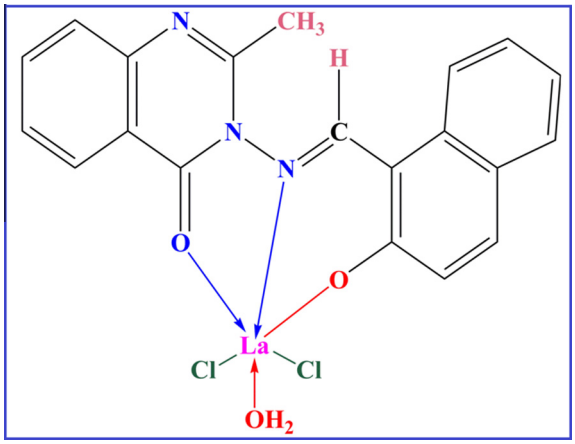

Fig. 1. Proposed structure of La(III) complex.

The mass spectra of newly synthesized compounds were in agreement with their structures. The proposed molecular formula of each compound was confirmed by its molecular formula weight with *m*/*z* values. The mass spectra of the Schiff's base HNMAMQ showed the formation of a molecular ion peak at *m*/*z* 329 $[M]^+$, whereas the La(III) complex shows the formation of a molecular ion peak along with an isotopic peak at *m*/*z* 556, 558 and 560 $[M]^+$, $[M+2]^+$ and $[M+4]^+$ corresponding to their molecular formula.

Thermal gravimetrical analysis (TGA) for the La(III) complex was carried out within a temperature range from room temperature up to 1000 °C under nitrogen atmosphere with a heating rate of 10 °C per min. The La(III) complex does not show weight

loss below 120 °C indicates the absence of lattice water. However, it undergoes four stages of decomposition as follows:

1. The initial weight loss of 3.28% (Cal. 3.23%) in the temperature range of 195–220 °C account for the loss of coordinated water molecule [29].
2. In the second step the resultant intermediate complex formed above, underwent further degradation with weight loss in the temperature range of 220–350 °C owing to the removal of chloride molecules (Obs. 13. 52%; Cal. 13.19%).
3. The third decomposition occurred with weight loss in the range of 350–420 °C corresponds to the loss of —C_9 H_7N_2O species (Obs. 34.10%; Cal. 34.04%).
4. The fourth decomposition occurred in the temperature range of 420–625 °C with a weight loss of 8.80% (Cal. 8.76%) which account for the loss of —HCN species.

Finally, the most stable oxide was formed, on further heating up to 1000 °C. The weight of the residue corresponds to the formation of the La_2O_3.

Antimicrobial activity of the Schiff's base HNMAMQ and its La(III) complex against MRSA

The Schiff's base HNMAMQ exhibit the good antimicrobial activity against MRSA with a zone of inhibition (15 mm) however, upon complex formation with La(III), its antimicrobial activity increase with a zone of inhibition (22 mm) as presented in supplementary file Figs. S2 and S3. From the results it was clear that the Schiff's base HNMAMQ alone and in complex formation with La(III) shows excellent antimicrobial activity.

The MIC of the Schiff's base HNMAMQ and its La(III) complex were varied from 5 to 50 μg/mL, which reveals that, La(III) complex registered the MIC value at (15 μg/mL) as an excellent antimicrobial agent over the Schiff base HNMAMQ (35 μg/mL) as compared with the standard methicillin antibiotic (15 μg/mL), as presented in supplementary file Table S1.

The antimicrobial activity of the Schiff's base was rationalized due to presence azomethine (>C=N) group which imports in elucidating the mechanism of transamination and resamination reactions in the biological system [30]. The formation of hydrogen bonds through the azomethine group with the active centers of various cellular constituents, resulting in interference with normal cellular processes [31]. Furthermore, it has also been suggested that the Schiff base ligands with nitrogen and oxygen donor systems might inhibit enzyme production causing cell death [32].

The enhanced activity of metal complex than Schiff's base can explained by Tweedy's chelation theory, which suggest that the chelation could allow for the delocalization of π-electrons over the entire chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity facilitates the penetration of the complexes into lipid membranes, further restricting proliferation of the microorganisms [33]. On the other hand, Chelation is not only the principle factor for antimicrobial activity since; it is expected to be a function of steric, electronic and pharmacokinetic factors along with mechanistic pathway. Other factors such as solubility, conductivity, dipole moment, size of metal ions, stability constants of the complexes and their magnetic moments are also reported to influence the microbial activity of the complexes [34].

Conclusion

In conclusion, herein we report the synthesis of new Schiff's base HNMAMQ and its La(III) complex. Formation of the compounds were confirmed through IR, NMR, mass spectra, and thermal studies which explain the participation of azomethine nitrogen, carboxylato oxygen and phenolic oxygen with La(III) ion. Upon complex formation, the Schiff's base HNMAMQ exhibit octahedral geometry with La(III) ion. The antimicrobial activity of the Schiff's base HNMAMQ and its La(III) complex were evaluated against clinically isolated MRSA, the MIC of the Schiff's base HNMAMQ was estimated 35 μg/mL, moreover the synergetic effect of the Schiff's base HNMAMQ and its La(III) complex increased the antimicrobial activity with MIC 15 μg/mL this could be explained due to chelation theory. The Schiff's base HNMAMQ alone and in combination with La(III) complex showed excellent antimicrobial activity the same can be used as a new antimicrobial agent to decrease the MRSA incidence and also may be in future, useful in the developing prospective pharmaceutical, and physiological implications in the field of medicinal chemistry.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.03.115.

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