



Preparation and characterization of new tetradentate Schiff base metal complexes and biological activity evaluation



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HIGHLIGHTS

- Four new complexes ciprofloxacin Schiff base were synthesized.
- The complexes were characterized by using spectroscopic methods.
- The antibacterial activity of ciprofloxacin Schiff base and their metal complexes were evaluated.

ARTICLE INFO

Article history:

Received 29 May 2013

Received in revised form 24 July 2013

Accepted 28 July 2013

Available online 2 August 2013

Keywords:

Tetradentate Schiff base
Transition metal complexes
Infrared
Mass spectra

ABSTRACT

A new Schiff base (N,N'-ethylene (bis 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazine-1-yl)-quinoline-3-carboxylic acid) and its Zn(II), Zr(IV), Ce(IV) and U(VI) complexes were synthesized and characterized by elemental analysis, molar conductance, IR, UV–Vis, ¹H NMR spectra, magnetic moment, thermal analysis as well as mass spectra. The IR results demonstrate that the tetradentate binding mode of the ligand involving azomethine nitrogen and carboxylato oxygen atoms. The calculated bond length and the bond stretching force constant, F(U=O), values for UO₂ bond are 1.744 Å and 654.49 N m⁻¹. The antimicrobial activity of the synthesized ligand and its complexes were screened and the results showed that the metal complexes were found to be more active than free ligand.

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1. Introduction

Metal-chelated Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition-metal coordination chemistry due to their preparative accessibility, diversity and structural variability [1,2]. Schiff base metal complexes attract considerable interest and occupy an important role in the development of the chemistry of chelate systems [3,4] due to the fact that especially these with N₂O₂ tetradentate ligands, such systems closely resemble metallo-proteins. Some Schiff base complexes are also used as model molecules for biological oxygen carrier systems [5] as well as having applications in analytical fields [6]. Complexation reactions of transition elements with Schiff bases have been studied extensively [7–11]. Survey of the literature reveals a very little work has appeared on complex formation of transition metals with fluoroquinolone drug Schiff base [12].

The present work deals with the preparation and characterization of ciprofloxacin Schiff base (CIP-en) (N,N'-ethylene (bis

1-cyclopropyl-6-fluoro-4-oxo-7-(piperazine-1-yl)-quinoline-3-carboxylic acid) followed by studying their complexation with di, tetra and hexavalent transition metal ions. Indeed, the biological activity of the ligand and its complexes were screened against selected kinds of bacteria and fungi.

2. Materials and methods

2.1. Chemicals

All chemicals used were of high purity grade and used without further purification. Ciprofloxacin hydrochloride was obtained from the Egyptian International Pharmaceutical Industrial Company (EIPICO). Ethylenediamine, glacial acetic acid, acetone, ethanol, NaOH, FeCl₃·6H₂O, BaCl₂, AgNO₃, FeSO₄, K₂CrO₄ were purchased from Fluka Chemical Co. Zn(NO₃)₂·6H₂O, ZrOCl₂·8H₂O (99.9%), UO₂(CH₃COO)₂·2H₂O and Ce(SO₄)₂ from Aldrich Chemical Co.

2.2. Synthesis of ligand (CIP-en) (C₃₆H₄₂N₈O₄F₂Cl₂)

An ethanolic solution of ciprofloxacin (2 mmol, 0.734 g) with ethylene diamine (1 mmol, 0.066 ml) was boiled under reflux in

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the presence of 0.5 ml glacial acetic acid separately for 4 h. The resulting solution was concentrated to 8 ml on a water bath and allowed to cool at 0 °C. White precipitate was filtered off, washed several times by ethanol and dried under vacuum over CaCl₂ in a desiccator. The proposed formula of the ligand (C₃₆H₄₂N₈O₄F₂Cl₂, M.wt. = 759) is in good agreement with mass spectrum (M⁺) at *m/z* = 758 (66.98%) and confirmed by IR spectral data. The ¹H NMR spectrum of the ligand in DMSO-d₆ showed signals at δ 11.0 ppm assigned to the proton of carboxylic (COOH).

2.3. Synthesis of metal complexes

The light brown solid complex [Zn(CIP-en)(H₂O)₂](NO₃)₂·7H₂O was prepared by adding 0.5 mmol (0.148 g) of Zn(NO₃)₂·6H₂O in 20 ml ethanol drop-wisely to a stirred suspended solution of CIP-en (0.5 mmol, 0.379 g) and NaOH (1 mmol, 0.04 g) in 50 ml ethanol. The reaction mixture was stirred for 15 h at 35 °C in a water bath. The light brown precipitate was filtered off and dried under vacuum over anhydrous CaCl₂. The light yellow, yellow and dark yellow solid complexes of [ZrO(CIP-en)Cl]Cl·9H₂O, [Ce(CIP-en)(H₂O)₂](SO₄)₂·6H₂O and [UO₂(CIP-en)](OCH₃CO)₂·6H₂O were prepared in a similar manner described above by using acetone as a solvent and using ZrOCl₂·8H₂O, Ce(SO₄)₂ and UO₂(CH₃COO)₂·2H₂O, respectively, in 1:1 molar ratio. All compounds were characterized by their elemental analysis, molar conductance, magnetic moment, IR, ¹H NMR, electronic, mass spectra as well as thermal analysis.

We did not manage to obtain a crystal of the complexes suitable for the structure determination with X-ray crystallography, although diverse crystallization techniques were used.

Elemental C, H, N and halogen analysis was carried out on a Perkin Elmer CHN 2400. The percentage of the metal ions were determined gravimetrically by transforming the solid products into metal oxide or sulfate and also determined by using atomic absorption method. Spectrometer model PYE-UNICAM SP 1900 fitted with the corresponding lamp was used for this purpose. IR spectra were recorded on FTIR 460 PLUS (KBr discs) in the range from 4000 to 400 cm⁻¹, ¹H NMR spectra were recorded on Varian Mercury VX-300 NMR Spectrometer using DMSO-d₆ as solvent. TGA–DTG measurements were carried out under N₂ atmosphere within the temperature range from room temperature to 800 °C using TGA-50H Shimadzu, the mass of sample was accurately weighted out in an aluminum crucible. Electronic spectra were obtained using UV-3101PC Shimadzu. The solid reflection spectra were recorded with KBr pellets. Mass spectra were recorded on GCMS-QP-1000EX Shimadzu (ESI-70ev) in the range from 0–1090. Magnetic measurements were carried out on a Sherwood scientific magnetic balance using Gouy method using Hg[Co(SCN)₄] as calibrant. Molar conductivities of the solution of the ligand and metal complexes in DMF at 1 × 10⁻³ M were measured on CONSORT K410. All measurements were carried out at ambient temperature with freshly prepared solution.

2.4. Antimicrobial investigation

Antibacterial activity of the ligand and its metal complexes was investigated by a previously reported modified method of Beecher and Wong [13] against different bacterial species, such as *Staphylococcus aureus* (*S. aureus*), *Bacillus subtilis* (*B. subtilis*), *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*P. aeruginosa*) and antifungal screening was studied against two species, *Candida albicans* and *Aspergillus fumigatus*. The tested microorganisms isolates were isolated from Egyptian soil and identified according to the standard mycological and bacteriological keys for identification of fungi and bacteria as stock cultures in the microbiology laboratory, Faculty of Science, Zagazig University. The nutrient agar medium for antibacterial was (0.5% Peptone, 0.1% Beef extract, 0.2% Yeast extract, 0.5%

NaCl and 1.5% Agar–Agar) and czapeks Dox medium for antifungal (3% Sucrose, 0.3% NaNO₃, 0.1% K₂HPO₄, 0.05% KCl, 0.001% FeSO₄, 2% Agar–Agar) was prepared [14] and then cooled to 47 °C and seeded with tested microorganisms. Sterile water agar layer was poured, solidified then pour, the prepared growth medium for fungi and bacteria (plate of 12 cm diameter, 15 ml medium plate). After solidification 5 mm diameter holes were punched by a sterile cork-borer. The investigated compounds, i.e., ligand and their complexes, were introduced in Petri-dishes (only 0.1 ml) after dissolving in DMF at 1.0 × 10⁻³ M. These culture plates were then incubated at 37 °C for 20 h for bacteria and for seven days at 30 °C for fungi. The activity was determined by measuring the diameter of the inhibition zone (in mm). Bacterial growth inhibition was calculated with reference to the positive control, i.e., Ampicillin, Amoxicillin and Cefaloxin.

3. Results and discussion

The analytical data of the ligand and its complexes along with some physical properties are summarized in Table 1. The ligand on interaction with Zn(II), Zr(IV), Ce(IV) and U(VI) ions yield complexes corresponding to the general formula [M(CIP-en)(H₂O)₂]^{m+} (M = Zn(II) and Ce(IV)), [ZrO(CIP-en)Cl]⁺ and [UO₂(CIP-en)]⁺². The complexes were characterized through their elemental analysis, IR, UV–Vis, ¹H NMR, melting point, molar conductivity, magnetic properties as well as thermogravimetric analyses. The results enable us to characterize the complexes and make an assessment of the bonding and structures inherent in them. All the prepared complexes contain water molecules and the number of bound water molecules in these complexes being different. The IR spectroscopic and thermogravimetric data confirm water in the composition of the complexes. Also, the molar conductance value of free (CIP-en) is 138.2 S cm² mol⁻¹ at room temperature and the corresponding values of the complexes at the same temperature were found to be in the range from 186.8 to 272.8 S cm² mol⁻¹. The higher molar conductance values of the complexes compared with the ligand reveal their electrolytic nature [15] (Table 1). The magnetic moments (as B.M.) of the complexes were measured at room temperature where Hg[Co(SCN)₄] were used a calibrant. The Zn(II), Zr(IV), Ce(IV) and U(VI) complexes are found in diamagnetic character with molecular geometries octahedral.

Qualitative reactions for the isolated complexes of Zn(II), Zr(IV), Ce(IV) and U(VI) revealed the presence of nitrate, chloride, sulfate and acetate ions as counter ions (outside the complexes sphere) and not coordinate, the complexes solution were tested with an aqueous solutions of ferrous sulfate, silver nitrate, barium chloride and ferric chloride a black ring (FeSO₄·NO) for Zn(II), a white precipitate for Zr(IV) and Ce(IV) and a red brown for U(VI) were formed [16]. This indicate that nitrate, chloride, sulfate and acetate ions are found as counter ions which in good agreement with the results of molar conductance and infrared data.

3.1. IR absorption spectra

The mid infrared spectra of CIP-en Schiff base and their metal complexes [Zn(CIP-en)(H₂O)₂](NO₃)₂·7H₂O, [ZrO(CIP-en)Cl]Cl·9H₂O, [Ce(CIP-en)(H₂O)₂](SO₄)₂·6H₂O and [UO₂(CIP-en)](OCH₃CO)₂·6H₂O were recorded from KBr discs. As expected, the absorption bands characteristic of CIP-en Schiff base acting as tetradentate unit in the complexes are observed with small changes in band intensities and wave number. Before discussing the assignments of the infrared spectra, the proposed structures of the complexes must be considered. Here, metal ions react with these tetradentate Schiff base forming complexes of monomeric structure where the metal ions is six coordinated [17,18] (Scheme 2).

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