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Metal complexes of Schiff base: Preparation, Characterization and Antimicrobial activity

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Abstract

The tridentate (HL) Schiff base was synthesized by reacting 2-quinolinecarboxaldehyde with 3-aminophenol in absolute ethanol. The resulting HL ligand was also coordinated with the Ni(II) and Cd(II) ions. This Schiff base and its Ni(II) and Cd(II) complexes were characterized by multiple and usual methods including the 1H NMR, elemental analysis, FT-IR, UV-Vis, and magnetic moments. It was found that the ligand acts as a tridentate chelate. Both compounds, HL ligand and its Ni(II), Cd(II) complexes were as well tested in biological activity. The obtained results indicate that the Ni(II) complex only exhibit antifungal activity and the two complexes have antibacterial activity towards the same organism studied.

Key words: Schiff base, UV-visible, magnetic moment, in vitro antimicrobial activity.

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1. Introduction

Schiff bases are considered as privileged ligands because they are easily prepared by condensation of aldehydes or ketones with amines [1]. Literature survey indicates that both Schiff base and their metal complexes have been successfully used in variety of applications such as synthetic chemistry, modern technology, corrosion inhibitors, oxidation catalysts and drug development [2].

In the present paper, Schiff base was synthesized by the condensation of 2-quinolinecarboxaldehyde and 3-aminophenol in ratio 1:1. Its mode of chelation with Ni(II) and Cd(II) ions was examined, as well as the characterization, spectroscopic techniques and antimicrobial activity studies of the Schiff base ligand and its metal complexes have been described.

2.Experimental

Materials and reagents

All chemical used were of (AR) grade and of highest purity available. The all chemicals and reagents were from Sigma-Aldrich (2-quinolinecarboxaldehyde and 3-aminophenol, $CdCl_2$), while $NiCl_2.6H_2O$ was supplied from BDH. Organic solvents such as ethyl alcohol (95%) and dimethyl formamide (DMF) were purchased from BDH. De-ionized water was usually used in all preparations.

Solutions of Schiff base HL and its metal complexes

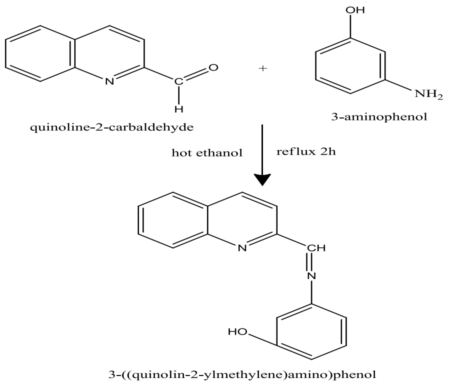
Fresh stock solutions of (10^{-3} M) HL was prepared by dissolving the accurately weighed amount of HL (0.4 g) in the appropriate volume of DMF. Stock solutions of the metal complexes (Ni(II) were 0.38 g/L, Cd(II) was 0.295 g/L) were prepared by dissolving the accurately weighed amounts of the metal complexes in the appropriate volume of DMF. The metal solutions were standardized by the recommended procedures.

Instrumentation

Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Egypt, using CHNS-932 (LECO) Vario Elemental Analyzer. Molar conductivites of (10^{-3} M) solutions of the solid complexes in DMF were measured using Jenway uolo conductivity meter. Electronic spectra were recorded at room temperature on a shimadzu 3101 pc spectrophotometer as solution in DMF. UV-Vis spectra were carried out on UV mini-1240, UV-Vis spectrophotometer Shiamdzu. FT-IR spectra were recorded on a perkin-Elmer 1650 spectrometer (4000 - 400 cm^{-1}) in KBr pellets. ^1H NMR spectra, as a solution in DMSO-d_6, were recorded on a 300 MHz varian-oxford Mercury at room temperature using TMS as an internal standard. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. The antimicrobial activity was carried out at the Microanalytical center, Cairo University, Egypt.

Synthesis of the Schiff base ligand

Novel Schiff base HL was synthesized using the recommended method. They were carried out by condensation of 3-aminophenol with 2-quinoline-carboxaldehyde. A solution of 2-quinoline carboxaldehyde (0.4 g) dissolved in DMF was added dropwise to 3-amino phenol (0.277 g) in 1:1 ratio dissolved in ethanol. The resulting mixture was stirred under reflux for about 3h during which an orange solid compound was separated. They were filtered, recrystallized and washed with diethylether and dried in vacuum.



Scheme (1): Synthesis of Schiff base ligand HL.

Schiff base ligand had an orange color (melting point 200 °C), yield 83%, molecular weight 248 g/mol with molecular formula $C_{16}H_{12}N_2O$. The elemental analysis was as follows % found (calcd.): C: 77.42 (77.48), H: 4.84 (4.91), N: 11.29 (11.49). FT-IR (ν, cm^{-1}): azomethine (C=N) 1616 m, C=N of pyridine ring 1597 m, (OH) stretching at 3273 br. UV-Vis (DMF): (λ_{max} nm) = 272 (π-π^*) and 353 (n-π^*). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 5.79 – 8.97 (m, 12H, Ar-H), 9.60 (s, 1H, azomethine), 10.20 (Ar- OH).

Synthesis of the Schiff base metal complexes

A hot DMF solution of Schiff base ligand (0.4 g) was added drop wise to 10 ml of the metal(II) chlorides [Ni(II): 0.382 g and Cd(II):0.295 g] in hot ethanol. The reaction took place in 1:1 mole ratio. The resulting mixture was stirred under reflux for 2h whereupon the complexes precipitated. The product obtained was filtered, washed with ethanol, diethyl ether and then dried in a vacuum over $CaCl_2$.

$[NiHLCl(H_2O)_2]Cl.4H_2O$

yield 86%; m.p ≥ 300 ˚C; dark brown solid. Anal. found for $C_{16}H_{24}Cl_2NiN_2O_7$ (%): C: 39.53, H: 4.94, N: 5.76, Ni: 12.08. Calcd. (%): C: 39.74, H: 4.99, N: 5.87, Ni: 12.28. Molar conductivity (Ω^{-1} mol^{-1} cm^2) = 61, FT-IR (ν, cm^{-1}): azomethine (C=N) 1653 sh, (C=N) of pyridine ring 1609 w, (M-N) 407 w, (M-O) 565 w, H_2O of coordinated water 935 w and 870 w, OH stretching 3429 m, UV-Vis (DMF): (λ_{max} nm) = 256 (π-π^*), 318 nm (n-π*) and 517 nm d-d transition.

$[CdHLCl_2\,H_2O].2H_2O$

yield 86%; m.p ≥ 300 ˚C; dark brown solid. Anal. found for $C_{16}H_{18}Cl_2CdN_2O_4$ (%): C: 39.55, H: 3.71, N: 5.77, Cd: 23.21. Calcd. (%): C: 39.61, H: 3.91, N: 5.82, Cd: 23.32. Molar conductivity (Ω^{-1} mol^{-1} cm^2) = 4, FT-IR (ν, cm^{-1}): azomethine (C=N) 1639 w, (C=N) of pyridine ring 1630 w, (M-N) 477 s, (M-O) 591 m, H_2O of coordinated water 830 w and 913 w, OH stretching 3428 br, UV-Vis (DMF): (λ_{max} nm) = 270 (π-π^*), 335 nm (n-π*) and 521 nm d-d transition. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 5.96 – 8.21 (m, 12H, Ar-H), 9.42 (s, 1H, azomethine), 10.32 (s, 1H, Ar-OH).

Antimicrobial activity

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method. 100 µl of the tested bacteria or fungi were grown in 10 ml of fresh media until they reached a count of approximately 108 cells/ml for bacteria and 105 cells/ml for fungi. 100 µl of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disc diffusion method. Of the many media available, NCCLS recommends Mueller-Hinton agar due to: it results in good batch-to-batch reproducibility. Disc diffusion method for filamentous fungi tested by using approved standard method (M38-A) developed. For evaluating the susceptibilities of filamentous fungi to antifungal agent. Disc diffusion method for yeast developed by using approved standard method (M44-P). Plates inoculated with Gram(+) bacteria as *Staphylococcus aureus* and *Bacillus subtilis*; Gram(-) bacteria as *Escherichia coli* and *Pseudomonas aeruginosa*, they were incubated at 35-37 ºC for 24-28 hours and yeast fungus as *Candida albicans* and *Aspergillus flavus* incubated at 30 ºC for 24-28 hours and then the diameters of the inhibition zones were measured in millimeters. Standard discs of amikacin (antibacterial agent) and ketokonazole (antifungal agent) served as positive controls for antimicrobial activity but filter discs impregnated with 10 µl of solvent (distilled water, chloroform and DMSO) were used as a negative control. The agar used is Meuller-Hinton agar that is rigorously tested for composition and pH. Further the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values. Blank paper disks (Schleicher and Schuell, spain) with a diameter of 8.0 mm were impregnated with 10 µl of tested concentration of the stock solutions. When a filter paper disc impregnated with a tested chemical is placed on agar, the chemical will diffuse from the disc into the agar. This diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar, it will not grow in the area around the disc if it is susceptible to the chemical. This area of no growth around the disc is known as zone of inhibition or clear zone. For the disc diffusion, the zone diameters were measured with slipping calipers of the national committee for clinical laboratory standards. Agar based methods such as E test and disc diffusion can be good alternatives because they are simpler and faster than broth-based methods.

3. Results and discussion

Characterization of Schiff base ligand

Schiff base ligand HL was prepared by the condensation of 2-quinolinecarboxaldehyde with 3-aminophenol in 1:1 ratio. The elemental analysis data obtained were in good agreement with those for the calculated formula indicated that the ligand had the molecular formula C16H12N2O

[15].

The FT-IR spectrum of HL showed a lack of one NH_2 stretching characteristic band of 3-aminophenol and C=O band of 2-quinolinecarboxaldehyde. A new sharp vibration band appeared at 1616 cm^{-1} due to azomethine group (C=N) and (C=N) of pyridine ring appeared at 1597 cm^{-1}, OH stretching band at 3273 cm^{-1} , indicated the formation of the Schiff base ligand HL [3]. The ^{1}H NMR spectrum was obtained to confirm the ligand structure and its purity. The singlet signal at 9.60 ppm was attributed to the azomethine CH proton. The multiplet 13H in the region at 5.79 – 8.97 ppm was attributed to the aromatic protons and the signal of OH proton at 10.20 ppm confirmed the formation of HL.

Characterization of metal complexes

Elemental analysis and molar conductance

The elemental analyses results were in close agreement with the theoretical values supporting the intended molecular formula and structures. The analytical results showed (1:1) metal ligand ratio, that is, ML type. The molar conductivity of Ni(II) complex was 61 Ω^{-1}.mol^{-1}.cm^{2} suggesting its electrolytic nature but the molar conductivity of Cd(II) complex was 4 Ω^{-1}.mol^{-1}.cm^{2} suggesting its non-electrolytic nature [4].

Electronic spectra

The electronic spectrum of the ligand (10^{-4} M) in DMF showed (π-π^*) transition at 272 nm and (n-π^*) transition at 353 nm. The (n-π^*) transitions was shifted to 318 nm in Ni(II) complex and disappeared in Cd(II) complex. The (π-π^*) transitions was shifted to 256 and 270 nm in Ni(II) and Cd(II) complexes, respectively. The spectrum also showed a d-d transitions at 517 nm in Ni(II) complex [5, 6].

Infrared spectral data

The IR spectra of Ni(II) and Cd(II) complexes with Schiff base revealed that the coordination between metal ions and ligand has occurred [14]. The strong band at 1616 cm^{-1} for free ligand is due to azomethine vibration (C=N). This band was shifted to higher frequency at 1653 and 1639 cm^{-1} in Ni(II) and Cd(II) complexes, respectively. The (OH) stretching band for free ligand was at 3273 cm^{-1}. This band was shifted to lower frequency at 3429 and 3428 cm^{-1} in Ni(II) and Cd(II) complexes, respectively [16]. The (C=N) of pyridine ring band for free ligand was at 1597 cm^{-1}. This band was shifted to higher frequency at 1609 and 1630 cm^{-1} in Ni(II) and Cd(II) complexes, respectively. The spectra of Ni(II) complex also showed stretching bands of the coordinated water at 870 and 935 cm^{-1}. The spectra of Cd(II) complex also showed stretching bands of the coordinated water at 830 and 913 cm^{-1}. Some new bands were appeared in the spectra of metal complexes at 565 and 591 cm^{-1} for υ(M-O) vibration and 407 and 477 cm^{-1} for υ(M-N) vibration in Ni(II) and Cd(II) complexes, respectively [7, 8]. From the IR data, it concluded that the ligand behaved as neutral tridentate ligand coordinating to the metal ion via azomethine N and pyridine ring N and protonated O of phenolic group.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of Cd(II) complex displayed all aromatic protons as multiplet in region 5.96 – 8.21 ppm (m, 12H, Ar-H), singlet signal at 9.41 ppm due to azomethine proton (CH=N) and phenolic proton at 10.32 ppm. ^{1}H NMR spectral data of Schiff base ligand and its Cd(II) complex confirmed the formation of Cd(II) complex with ligand. Accordingly, this clearly confirmed that the phenolic group coordinate with metal ion in the complex in the protonated form which confirm the IR finding [2, 9].

Magnetic moment measurements

The electronic spectrum of Ni(II) complex gave three bands in the 15, 860, 18, 523 and 29, 055 cm^{-1} regions corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ transitions, respectively. The observed magnetic moment of Ni(II) complex at room temperature was 3.32 BM. This value is in tune with a high spin configuration and showed the presence of an octahedral environment around the Ni(II) ion [10]. Cd(II) complex was diamagnetic and was likely to be of octahedral structures] 11]. From this it can be concluded that the Schiff base ligand under study was coordinated to the metal centers and the complexes were of octahedral geometry [10].

Structural Interpretation

According to all previous physicochemical studies and spectral analysis data the structures of the ligand and Ni(II) and Cd(II) complexes had been confirmed and the proposed structural formulae of the complexes were shown in Figure 1. These results lead to general formulae] $NiHLCl(H_2O)_2]Cl.4H_2O$ and $[CdHLCl_2(H_2O)\,]2H_2O$.

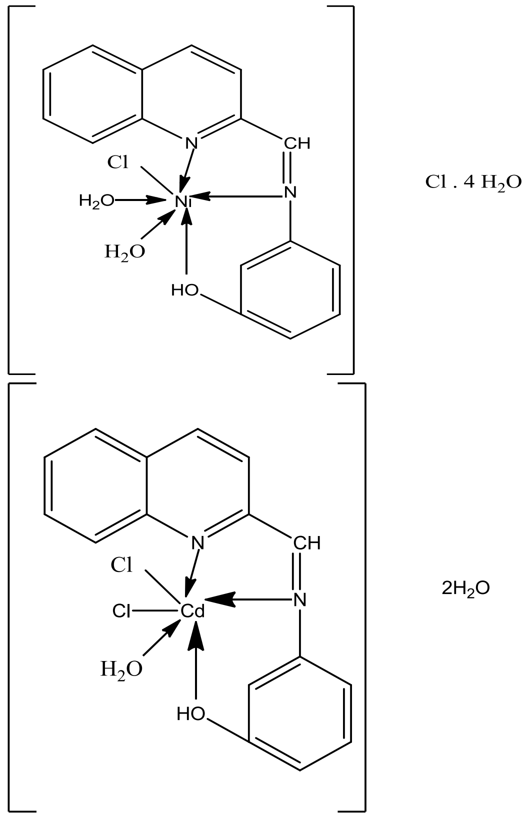


Fig (1): The proposed structures of the complexes of the Schiff base ligand (HL).

Biological Activity

Antimicrobial activity

The Schiff base as well as its Ni(II) and Zn(II) complexes were screened in vitro in order to evaluate their antimicrobial activity against G(-), G(+) bacteria and fungi and compared to amikacin used as antibacterial standard and ketokonazole as antifungal standard [12]. The results showed that, using Gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*), the Ni(II) and Cd(II) complexes have higher antibacterial activity than that of the free ligand and the Cd(II) complex has the highest activity.

Using Gram-negative bacteria (*Pseudomonas aeruginosa*, *Escherichia coli)*, the Ni(II) and Cd(II) complexes have higher activity than that of the free ligand and the Cd(II) has the highest activity [17].

The Antifungal studies showed, Using *Aspergillus flavus* and *Candida albicans*, the free ligand does not have any antifungal activity against it, but Ni(II) and Cd(II) complexes have antifungal activity [18].

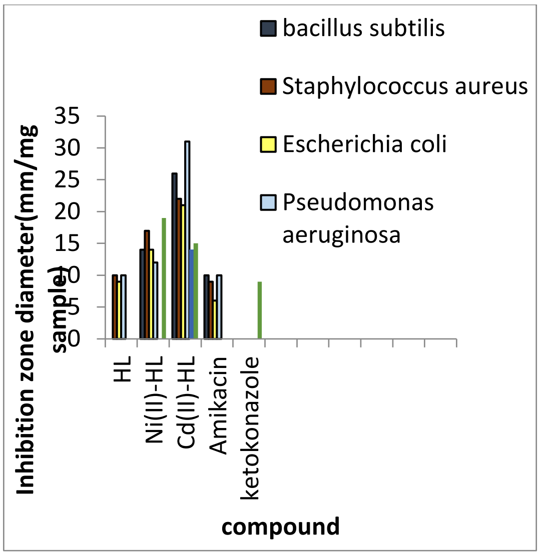


Fig (2): Biological activity of Schiff base ligand (HL) and Ni(II) and Cd(II) complexes against different bacterial and fungal species.

4. Conclusion

The Ni(II) and Cd(II) Schiff base complexes were prepared by using tridentate 2-quinolinecarboxaldehyde based Schiff base ligand derived from the reaction of 2-quinolinecarboxaldehyde with 3-aminophenol. The Schiff base ligand reacted to metal ions in 1:1 molar ratio. Ni(II) complex was electrolyte but Cd(II) complex was non-electrolyte. The complexes were octahedral and the coordination to metal occurred through the phenol, imine and pyridine moieties. The complexes had higher antimicrobial activity than that of the free Schiff base ligand and the Cd(II) had the highest activity.

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