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Synthesis and characterization, antimicrobial activity, DNA binding and DNA cleavage studies of new 5-chloro-2-[4-phenylthiazol-2-yl-iminomethyl]phenol metal complexes

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HIGHLIGHTS

- Novel Schiff's base complexes were synthesized.
- The complexes are characterized by different spectroscopic techniques.
- Structure and spectra for the ligand and its metal (II/III) complexes were computed at the B3LYP/6-31G(d).
- Ligand and its metal (II) complexes showed variable antimicrobial activities.
- The complexes display good DNA binding and DNA cleavage activity.

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ABSTRACT

New Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) complexes derived from bidentate Schiff base ligand, 5-chloro-2-[4-phenylthiazol-2-yl-iminomethyl]phenol (HL) have been synthesized. The molar ratio for all synthesized complexes is M: L = 1:2 which was established from the results of chemical analysis. The complexes have been characterized by elemental analysis, spectral (IR, UV–Vis, (^{1}H and ^{13}C) NMR, mass, ESR, XRD, CV, fluorescence, and magnetic as well as thermal analysis measurements. The IR spectra of the prepared complexes were suggested that the Schiff base ligand behaves as a bi-dentate ligand through the azomethine nitrogen atom and phenolic oxygen atom. The crystal field splitting, Racah repulsion and nepheloauxetic parameters and determined from the electronic spectra of the complexes. The presence of co-ordinated water molecules were confirmed by thermal studies. The spectroscopic studies suggest the octahedral geometry. From the modeling studies, the bond length, bond angle, core–core interaction, heat of formation, electronic energy, binding energy, HOMO, LUMO and dipole moment had been calculated to confirm the geometry of the ligand and their investigated complexes. Also, the thermal behavior and the kinetic parameters of degradation were determined using Coats–Redfern, Horowitz–Metzger and Piloyan–Novikova methods. Moreover, the in vitro antibacterial studies of all compounds screened against pathogenic bacteria (two Gram +ve and three Gram −ve) and three antifungal to assess their inhibiting potential. The assay indicated that the inhibition potential is metal ion dependent. The interaction of the complexes with calf thymus DNA (CT-DNA) has been investigated by UV absorption method, and the mode of CT-DNA binding to the complexes has been explored. Furthermore, the DNA cleavage activity by the complexes was performed.

Introduction

The condensation of primary amines with carbonyl compounds yields Schiff bases [1,2]. Schiff base with donors (N, O, S, etc) have structure similarities with neutral biological systems and due to presence of imine group are utilized in elucidating the mechanism of transformation of rasemination reaction in biological system [3–5]. Thiazole and its derivatives as ligands with potential sulfur and nitrogen bands are interesting and have gained special attention not only the structural chemistry of their multifunctional coordination modes but also of their importance in medicinal and pharmaceutical field. They show biological activities including

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antibacterial antifungal [6], antidiabetic [7], antitumor [8], antiproliferative [9], anticancer [10], herbicidal [11]. Schiff bases represent an important class of compounds because they are utilized as starting materials in the synthesis of industrial products [12].

Moreover, Schiff bases are regarded as privileged ligands [13]. Due to their capability to form complexes with different transition metals can act as catalysts for many different reactions [14,15].

The present work is focused on preparation, structural elucidation and antibacterial activity of a new Schiff base, 5-chloro-2-[4-phenylthiazol-2-yl-iminomethyl]phenol (HL) as well as its complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) metal ions.

Experimental

Synthesis of the Schiff base ligand (HL)

An mixture of ethanolic solution of 4-chloro-2-hydroxybenzaldehyde (3.89 g, 24.88 mmol) and 4-phenylthiazol-2-amine (4.38 g, 24.88 mmol) was refluxed for 15 h. The color of the reaction mixture was changed from pale yellow to brown color with the formation of a brown precipitate. The resulting solution was then concentrated by evaporation and filtered to isolate a solid brown Schiff base which washed several times with ethanol. The crystals were suction filtered washed with diethyl ether and dried in vacuum. The purity of the product was checked was by TLC. Yield: 88% and the melting point is 138 °C (Table 1).

Synthesis of metal complexes [1–7]

The apple-green $[Cr(L)_2(H_2O)Cl]0.5H_2O$ complex was prepared by adding chromium chloride hexahydrate, $CrCl_3{\cdot}6H_2O$, (0.133 g, 0.5 mmol) in 20 ml ethanol drop wisely to a stirred solution of HL (0.31 g, 1 mmol) in 50 ml ethanol. The reaction mixture was stirred for 3 h at room temperature. The apple-green precipitate was filtered off and dried under vacuum over $CaCl_2$. The orange–red, cannery–yellow, green, dark-green, dark brown and orange solid complexes of $[Cr(L)_2(H_2O)Cl]2H_2O$, $[Mn(L)_2(H_2O)_2]1.5H_2O$, $[Fe(L)_2(H_2O)Cl]2H_2O$, $[Co(L)_2(H_2O)_2]2H_2O$, $[Ni(L)_2(H_2O)_2]2H_2O$, $[Cu(L)_2(H_2O)_2]$-$2H_2O$, and $[Cd(L)_2(H_2O)_2]H_2O$ were prepared in a similar manner described above by using ethanol as a solvent and $CrCl_3.6H_2O$, $MnCl_2$, $FeCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, and $CdCl_2{\cdot}2.5H_2O$, respectively, in 1:2 M ratio (Table 1).

Physical measurements

Elemental analyses (CHNS) were carried out on a Perkin Elmer CHNS 2400 and chloride present in the complexes was estimated by Volhard's method [16]. 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. The molar conductance of solid chelates in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, $E = 3406$). Their IR spectra were recorded on Perkin–Elmer FT-IR spectrophotometer in Nujol mull and polyethylene pellets. The UV–visible absorption spectra were recorded using Jasco V-350 recording spectrophotometer at room temperature. Magnetic susceptibility of the metal complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alpha products, model MKI magnetic susceptibility balance and the effective magnetic moments were calculated using the relation $\mu_{eff} = 2.828\,(\chi_m{\cdot}T)^{1/2}$B.M, where χ_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GC–MS Hewlett–Packard instrument in the Microanalytical Center, Cairo University. The ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using 300 MHz Varian–Oxford Mercury. The deuterated solvent used was dimethylsulphoxide (DMSO) and the spectra extended from 0 to 15 ppm. Electrochemical behavior of the metal complexes was investigated with CH Instruments, U.S.A (Model 1110A-Electrochemical analyzer, Version 4.01) in HPLC grade DMF containing n-Bu_4NClO_4 as the supporting electrolyte. The three-electrode system consisted of glassy carbon electrode (3 mm diameter) as a working electrode, a Ag/AgCl (3 M KCl) reference electrode and a platinum wire as auxiliary electrode was used. In order to provide a reproducible active surface and to improve the sensitivity and resolution of the voltammetric peaks, the glassy carbon electrode was polished to a mirror finish with 0.3 μm alumina on a smooth polishing cloth and then rinsed with methanol and double distilled water prior to each electrochemical measurements. The electrode cleaning procedure requires less than 3 min. All the solutions examined by electrochemical techniques were purged for 10 min with water-saturated nitrogen. All measurements were carried out at room temperature (24 °C).

Computational methods

We performed cluster calculations using DMOL^3 program [17] in Materials Studio package [18], which is designed for the realization

Table 1
Elemental analysis and physico-analytical data for HL and its metal complexes.

Compound no. M. F. [M Wt]	m.p. (°C)	Color [yield (%)]	Elemental analyses% calculated (found)						$^a\Lambda_m$
			M	C	H	N	S	Cl	
[HL] $C_{16}H_{11}ClN_2OS$ [314.79]	138	Brown [88]	–	61.05 (61.05)	3.52 (3.44)	8.90 (8.25)	10.19 (10.19)	11.26 (11.26)	–
(1)$[Cr(L)_2(H_2O)Cl]0.5H_2O$ $C_{32}H_{23}Cl_3CrN_4O_{3.5}S_2$ [742.03]	189	Apple-green [89]	7.01 (7.00)	51.80 (51.05)	3.12 (3.11)	7.55 (7.45)	8.64 (8.54)	14.33 (14.27)	20.20
(2)$[Mn(L)_2(H_2O)_2]1.5H_2O$ C C $_{32}H_{27}Cl_2MnN_4O_{5.5}S_2$ [745.55]	192	Orange–red [90]	7.37 (7.36)	51.55 (51.53)	3.65 (3.64)	7.51 (7.50)	8.60 (8.58)	9.51 (9.46)	17.33
(3)$[Fe(L)_2(H_2O)Cl]2H_2O$ $C_{32}H_{26}Cl_3FeN_4O_5S_2$ [772.91]	188	Cannery-yellow [88]	7.23 (7.22)	49.73 (49.73)	3.39 (3.32)	7.25 (7.23)	8.30 (8.28)	13.76 (13.64)	18.05
(4)$[Co(L)_2(H_2O)_2]2H_2O$ $C_{32}H_{28}Cl_2CoN_4O_6S_2$ [758.73]	186	Green [91]	7.77 (7.73)	75 50.67 (50.63)	3.72 (3.70)	7.39 (7.32)	8.45 (8.43)	9.35 (9.33)	16.53
(5)$[Ni(L)_2(H_2O)_2]2H_2O$ $C_{32}H_{28}Cl_2N_4NiO_6S_2$ [658.21]	193	Dark green [90]	7.74 (7.73)	50.68 (50.66)	3.72 (3.71)	7.39 (7.34)	8.46 (8.45)	9.35 (9.34)	15.55
(6)$[Cu(L)_2(H_2O)_2]2H_2O$ $C_{32}H_{28}Cl_2CuN_4O_6S_2$ [763.17]	197	Dark brown [84]	8.33 (8.32)	50.36 (50.35)	3.70 (3.70)	7.34 (7.33)	8.40 (8.38)	9.29 (9.22)	10.12
(7)$[Cd(L)_2(H_2O)_2]H_2O$ $C_{32}H_{26}Cl_2N_4O_5S_2Cd$ [794.02]	187	Orange [88]	14.16 (14.14)	48.40 (48.38)	3.30 (3.29)	7.06 (7.00)	8.08 (8.07)	8.93 (8.92)	10.25

[a] Λ_m: molar conductance (Ω^{-1} mo^{-1} cm^2).