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Thermal analyses data and antimicrobial screening of some new nano-structure five coordinated cadmium complexes

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ABSTRACT

In this work, synthesis of some nano-structure five coordinated cadmium complexes of a new tridentate Schiff base ligand (L) under ultrasonic conditions is presented. The ligand and its cadmium complexes were characterized by various analyses such as FT-IR, UV–visible, ^{1}H and ^{13}C NMR spectra, XRD, SEM and TEM. According to applied techniques, the general formula of $CdLX_2$ (X = Cl^-, Br^-, I^-, SCN^- and N_3^-) was suggested for the complexes. SEM, TEM and XRD analyses indicated that all complexes have nano-structure size in the range of 20–60 nm. In the next step, ligand and its cadmium complexes were subjected for *in vitro* antibacterial activities against two Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) and two Gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*). Moreover *in vitro* antifungal properties of the compounds against *Candida albicans* and *Aspergillus niger* were investigated. The results indicated that all compounds show acceptable antibacterial and antifungal activities. Furthermore, the interaction of these complexes with DNA indicated that both ligand and its complexes can destruct the DNA structure. In final, thermal behaviors of all compounds were studied by TG/DTG/DTA analysis data. The thermo-diagrams showed that the compounds are decomposed *via* 2–3 temperature stages. Some thermo-kinetic activation data including Arrhenius constant, ΔE^*, ΔH^*, ΔS^* and ΔG^* of each thermal decomposition step were estimated graphically by use of experimental TGA data based on the Coats–Redfern equation.

1. Introduction

In recent decades, using of metal-based compound in different medical fields has been increased [1–5]. The emergence of bacteria resistant to the current organic-based drugs and requirement to discovery of novel compounds for new therapeutic purpose are two important reasons attracting special attention of researchers to new biological active compounds [6,7]. Metal coordination compounds have some features such as types and number of ligand, coordination geometry, oxidation state of metal, outer sphere interaction and ligand exchange that can be used in design of therapeutic and diagnostic agents with especial characteristics [8]. Among metal-based compound, Schiff base metal complexes have been extensively investigated because of their potential for applications as catalyst and/or as industrial and pharmaceutical materials [9–11]. There are many reports on cadmium complexes with various structure and biological properties [12–14]. The study of biological properties of various Schiff base complexes has shown that these compounds have a broad spectrum of biological activities such as antibacterial [15], antiviral [16], anti-cancer [17], antifungal [18], anti-inflammatory [19] and anti-HIV [20]. Controlling the size of materials at the sub-micrometer scale is important in nanotechnology point of view that is dependent on synthetic reaction conditions [21–24]. Nano-structure size metal coordination compounds are fascinating to investigate because of their unique properties that are absolutely different from those in a bulk status relating to the large number of surface molecules. Nano-structure complexes generally are used as precursor for synthesis of nano-structure metal oxides. Also it has found that some properties of nano-structure compounds are improved with respect to bulk ones. In this direction, some nanostructure cadmium complexes and their applications have been reported in the literature [25,26].

In continuation of our previous studies [27–31], herein we report the synthesis and characterization of some new

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nano-structure five coordinated cadmium halide complexes of a new tridentate Schiff base ligand entitled as (9E)-N-((E)-3-phenylallylidene)-2-(2-styrylimidazolidin-1-yl)ethanamine(L). Furthermore, we investigated antibacterial/antifungal properties and DNA cleavage potentials of the titled compounds. Moreover, thermal behaviors (TG/DTG/DTA) of titled compounds were studied. Finally, some thermo-kinetic activation parameters for thermal decomposition processes were calculated graphically based on the Coats–Redfern relationship.

2. Experimental

2.1. Materials

All chemical reagents and solvents were purchased from the Merck, Aldrich and/or BDH chemical Companies in high purity. Cadmium azide and thiocyanate were freshly prepared based on our previous report [31].

2.2. Instrumentation analysis

The FT/IR spectra of all compounds were recorded on a JASCO-FT/IR680 instrument in the range of 4000–400 cm^{-1} as KBr discs. A Bruker DPX FT/NMR-400 was used for recording of ^{1}H and ^{13}C NMR spectra of the ligand and its cadmium complexes in DMSO-d_6. Melting points or decomposition temperatures were determined by BUCHI B-545 instrument. Molar conductivities of the compounds in chloroform were obtained by Metrohm-712 conductometer with a dip-type conductivity cell made of platinum black at room temperature. Thermo-diagrams (TG/DTG/DTA) were recorded by a Perkin-Elmer Pyris model instrument. For recording of electronic spectra of the compounds in the range of 200–800 nm, a JASCO-V570 spectrophotometer instrument was applied. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-1460 field emission scanning electron microscope using Ac voltage of 15 kV. TEM images were recorded on instruments of Philips CM-10 TEM microscope operated at 100 kV. X-ray powder diffraction (XRD) spectra were taken on a STOE type STIDY-MP-Germany X-ray diffractometer with Cu Kα radiation (λ = 1.5418). The high-power ultrasonic cleaning unit Bandelin Super Sonorex RK-100H with ultrasonic peak output 320 W and HF power 80 Weff has been used for ultrasonically synthesis of the complexes.

2.3. Synthesis of Schiff base ligand (L)

Preparation of ligand was done by gradually addition of 1 mmol (0.1032 g) of diethylenetriamine (in 10 mL ethanol) to 2 mmol (0.2643 g) of (E)-3-phenylprop-2-enal dissolved in ethanol (10 mL) under severe stirring for 4 h at room temperature. After evaporation of solvent, the ligand was obtained as yellow viscous oil. For purification of ligand, the oily product was washed twice with *n*-hexane.

2.4. Synthesis of nano-structure cadmium complexes

An ethanol solution of the Schiff base ligand (1 mmol in 20 mL) was gradually (during 20 min) poured into an ethanolic solution of cadmium halide, thiocyanate and/or azide salts (1 mmol in 20 mL) under ultrasonic irradiation. After complete addition, the reaction mixture was kept in the ultrasonic bath for a period of 60 min. The obtained precipitates were filtered and dried under vacuum.

2.5. Synthesis of five coordinated cadmium complexes (bulk)

For the synthesis of cadmium complexes, the ligand solution (1 mmol in 15 mL of ethanol) was drop by drop added to the stoichiometric amount of cadmium halide, thiocyanate and/or azide salts in ethanol (10 mL) during 10 min under vigorous stirring. Then, the reaction mixture was stirred more for 1–3 h at room temperature. Finally, the obtained precipitate of complexes was filtered and washed with ethanol several times. The resultant compounds were placed at 70–100 °C under vacuum and then kept in a desiccator over silica gel. Some important physical and spectral data (IR and UV–visible) have been tabulated in Tables 1 and 2.

The ^{1}H and ^{13}C NMR data of ligand and its cadmium complexes based on Scheme 1 are listed as seen in following:

Ligand (L): ^{1}H NMR (in DMSO): 7.79(d, $1H_f$, J = 10.02 Hz), 7.76(dd, $2H_c$, J = 6.80 Hz, J = 3.30Hz), 7.61(bd, $2H_{c'}$, J = 7.49Hz), 7.48(m, $7H_{bb',aa',e'}$), 7.11(d, $1H_d$, J = 16.22Hz), 7.00(d, $1H_{d'}$, J = 16.21Hz), 6.87(dd, $1H_e$, J = 15.96Hz, J = 7.59Hz), 4.05(m, $1H_{f'}$), 3.98(m, $2H_{g'}$), 3.89(m, $2H_{h'}$), 3.82(m, $2H_h$), 3.74(bs, $2H_g$), 3.19(bs, $1H_{NH}$) ppm. ^{13}C NMR (in DMSO): 167.02(C_7), 146.79($C_{5,5'}$), 131.22($C_{4,4'}$), 129.07($C_{1,1'}$), 128.72($C_{2,2'}$), 128.49($C_{3,3'}$), 127.47($C_{6,6'}$), 108.37($C_{7'}$) 55.52($C_{9'}$), 49.87(C_9), 43.63(C_8), 42.37($C_{8'}$) ppm.

[$CdLCl_2$]: ^{1}H NMR (in DMSO): 8.34(d, $2H_{f,f'}$, *J* = 8.99 Hz), 7.68(d, $4H_{c,c'}$, *J* = 6.98 Hz), 7.45(m, $6H_{b,b',a,a'}$), 7.27(d, $2H_{d,d'}$, *J* = 15.67 Hz), 7.97(dd, $2H_{e,e'}$, *J* = 15.92 Hz, *J* = 8.75 Hz), 3.63(bs, $5H_{h,h',NH}$), 2.87(bs, $2H_{g,g'}$) ppm. ^{13}C NMR (in DMSO): 167.57($C_{7,7'}$), 144.83($C_{5,5'}$), 135.32($C_{4,4'}$), 129.92($C_{1,1'}$), 129.04($C_{2,2'}$), 127.65($C_{3,3'}$), 126.97($C_{6,6'}$), 57.07($C_{8,8'}$), 47.87($C_{9,9'}$) ppm.

[$CdLBr_2$]: ^{1}H NMR (in DMSO): 8.36(d, $2H_{f,f'}$, *J* = 9.25 Hz), 7.67(d, $4H_{c,c'}$, *J* = 6.74 Hz), 7.45(m, $6H_{b,b',a,a'}$) 7.27(d, $2H_{d,d'}$, *J* = 15.93 Hz), 7.89(dd, $2H_{e,e'}$, *J* = 15.41 Hz, *J* = 9.51 Hz), 3.83(bs, $1H_{NH}$) 3.65(bs,

Table 1
Analytical and physical data of the tridentate Schiff base ligand and its Cd(II) complexes.

Run	Compounds	Color	M.P (Dec.) (°C)	Yield (%)	Λ°_{M} ($cm^2\,\Omega^{-1}\,M^{-1}$)
1	Ligand	Orange	Oil	95	0.006
2	$CdLCl_2$	Cream	179	89	0.015
3	$CdLBr_2$	Cream	217	92	0.017
4	$CdLI_2$	Yellow	177	94	0.21
5	$CdL(NCS)_2$	Yellow	120	87	0.014
6	$CdL(N3)_2$	White	247	62	0.018

(Dec.) refers to decomposition temperature of the compound.

Table 2
Vibrational (cm^{-1}) and electronic (nm) spectral data of tridentate Schiff base (L) and its cadmium(II) complexes.

Compound	νCH_{arom}	$\nu N–H_{amine}$	νCH (alkene)	νCH (aliph.)	νCH (imine)	$\nu(SCN/N_3)$	$\nu C{=}N$	$\nu C{=}C$	$\nu M–N$	λ_{max} (nm) (ε, $cm^{-1}\,M^{-1}$)
Ligand	3056	3245	3025	2925	2834	–	1635	1492–1450	–	228 (33,951), 281 (30,840)
$CdLCl_2$	3052	3218	3018	2910	2867	–	1632	1488–1448	506	262 (48,566), 288 (47,869)
$CdLBr_2$	3052	3210	3014	2906	2861	–	1632	1488–1448	505	261 (34,306), 290 (25,135)
$CdLI_2$	3050	3226	3023	2915	2865	–	1631	1490–1448	507	231 (41,235), 296 (48,087)
$CdL(NCS)_2$	3055	3236	3023	2918	2866	2061	1631	1489–1449	507	231 (21,242), 299 (40,175)
$CdL(N_3)_2$	3054	3210	3023	2927	2877	2063	1632	1488–1469	509	258 (46,593), 288 (46,084)

(ε) refers to absorption coefficient.