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Synthesis and Spectroscopic Characterization of Indomethacin–Cd(II), Ce(III), and Th(IV) Complexes: IR, ^{1}H NMR, Thermal, and Biological Studies[1]

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Abstract—Solid complexes have been prepared and characterized by IR, UV-Vis, elemental analysis, and ^{1}H NMR. Indomethacin forms complexes with Cd(II), Ce(III), and Th(IV) ions in molar ratios (ligand : metal) (2 : 1), (3 : 1), and (4 : 1), respectively. The IR spectra of the complexes suggest that the Indomethacin behaves as a monobasic monodentate ligand coordinated to the metal ions via the deprotonated carboxylate group. Prepared complexes exhibit higher antimicrobial activity against several microorganisms, compared to free ligand.

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INTRODUCTION

Indomethacin (Fig. 1) is one of the so called non-steroid anti-inflammatory drug which used to treatment fever, pain, stiffness, and swelling [1]. Indomethacin is a good chelating agent because it contains carboxylic group [2–4]. The metal carboxylates systems have an important role in inorganic and bioinorganic chemistry [5, 6]. There are many metal ions involved in various biological processes as a component of several metal-drug interactions [7–16]. It is a fact that metal complexes may be more active than the parent free ligand. Relatively small number of papers concerning the association between indomethacin ligand and metal ions can be found in the literature [17–23]. Complexes of ruthenium ions and some of non-steroidal anti-inflammatory drugs like ibuprofen, aspirin, naproxen and indomethacin were synthesized and characterized using various spectroscopic methods [17]. Two Sn(IV) indomethacin complexes have been prepared and structurally characterized by means of ^{119}Sn Moessbauer, vibrational, and NMR (^{1}H and ^{13}C) spectroscopy [18]. It was found that tin atoms are bridged by bidentate carboxylate ligands and by a monoatomic bridging oxygen [19]. The crystal and molecular structures of the ternary copper–indomethacin complexes were reported [20]. The interaction between indomethacin anions and heavy metal ions, such as Cd(II), Zn(II) and Cu(II), was studied in aqueous solution by polarographic techniques [21, 22]. Copper complex of indomethacin was found to be more effective than the parent drug against *Staphylococcus aureus* and *Escherichia coli* bacteria [23]. The goal of this research was to get a wider understanding of the structural and spectral properties as well as microbial activities of indomethacin-Cd(II), Ce(III), and Th(IV) complexes. Metallo-indomethacinate complexes were investigated by a number of spectral and thermal techniques.

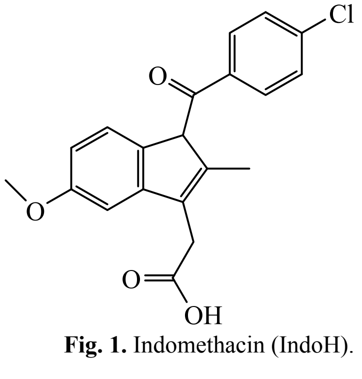

Fig. 1. Indomethacin (IndoH).

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[1] The text was submitted by the authors in English.

Table 1. Elemental analyses and physical data of Indo-Cd(II), Ce(III), and Th(IV) complexes

Comp. no.	M_W (g/mol)	C, %		H, %		N, %		M, %		Λ, Ω^{-1} cm^2 mol^{-1}
		found	calculated	found	calculated	found	calculated	found	calculated	
I	880	51.05	51.80	4.28	4.09	2.99	3.18	12.43	12.77	8.60
II	1264.47	53.93	54.09	3.67	4.03	2.85	3.32	11.55	11.08	13.00
III	1784	50.83	51.12	4.36	4.15	2.66	3.13	13.35	13.00	18.00

EXPERIMENTAL

All chemicals used were of the purest laboratory grade (Merck). $CdCl_2 \cdot H_2O$, $CeCl_3 \cdot 7H_2O$, $Th(NO_3)_4 \cdot 5H_2O$, were used for the preparation of the corresponding complexes. Indomethacin was received from Egyptian international pharmaceutical industrial company (EIPICO). CHN contents were determined using a Perkin–Elmer CHN 2400 analyzer. Metal content was found gravimetrically by converting the compounds into corresponding oxides. Molar conductivities of freshly prepared 1.0×10^{-3} mol/L DMSO solutions of complexes were measured using Jenway 4010 conductivity meter. IR spectra were recorded on a Bruker FTIR spectrophotometer (4000–400 cm^{-1}) in KBr pellets. UV-Vis spectra were recorded DMSO solvent with concentration (1.0×10^{-3} M) for the free Indo ligand and their complexes using Jenway 6405 spectrophotometer with 1 cm quartz cell, in the range of 200–800 nm. Solid reflectance spectra were performed on a Shimadzu 3101 pc spectrophotometer. ^{1}H NMR spectra of the free Indo ligand and their complexes were recorded on a Varian Gemini 200 MHz spectrophotometer using DMSO-d_6 as solvent and TMS as an internal reference. Thermogravimetric analysis (TG and DTG) was carried out in the temperature range from 25 to 800°C in nitrogen atmosphere on a Shimadzu TG 50H thermal analyzer. The experimental conditions were: platinum crucible, nitrogen atmosphere with a 30 mL/min flow rate, heating rate 10°C/min. Hole well method was used for the evaluation of antibacterial and antifungal activities of synthesized compounds.

Synthesis of Indo complexes. Target complexes were prepared using a ligand : salt molar ratio 1 : 2, 1 : 3, and 1 : 4 for Cd(II), Ce(III), and Th(IV) complexes, respectively. A solution of 0.5 mmol, 0.33 mmol and 0.25 mmol of appropriate salt (for Cd(II), Ce(III), and Th(IV) complexes, respectively), in 10 mL of distilled water was added to a solution of 1.0 mmol of Indomethacin in 20 mL of methanol under stirring. The pH of each solution was adjusted to 7–9 using 5% alcoholic ammonia solution. The resulting solutions were heated at 50°C for one hour and left to evaporate slowly at room temperature overnight. Precipitates obtained were filtered off, washed with hot water and then dried at 60°C. Elemental analysis data for the complexes are given in the Table 1.

RESULTS AND DISCUSSION

Molar conductivities of metal chelates of IndoH. The molar conductivity values for the Cd(II), Ce(III), and Th(IV) complexes of IndoH in DMF solutions (1.0×10^{-3} M) were found to be in the range of 8.60–18.00 Ω^{-1} cm^2 mol^{-1}, suggesting them to be non-electrolytes as shown in Table 1. The conductivity measurements play an important role in detection the place of counter ions inside or outside the coordination sphere. This method testing the degree of ionization of the complexes comparing to the free ligands, with the higher molar conductance value corresponding to the presence of counter ions outside the coordination sphere and vice versa [24]. Under this prediction, it is clear from the obtained data that all three Cd(II), Ce(III), and Th(IV) complexes seem to be non-electrolytes. Also the molar conductance values indicate that the anions are absent or exhibited inside the coordination sphere. The fact that Cl^- ions were not detected by addition of $AgNO_3$ solution to the solutions of the complexes in nitric acid matches well this conclusion.

Infrared spectra of IndoH and its Cd(II), Ce(III), and Th(IV) complexes. The IR data for IndoH and its complexes are listed in Table 2 and shown in Fig. 2 (as example, for Ce(III) complex **II**). The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may involved in chelation. There are some guide peaks in the spectra of the ligand, which are useful in achieving this goal. The position and/or the intensities of these peaks are expected to change upon chelation. These guide peaks

Table 2. IR frequencies (4000–400 cm^{-1}) of IndoH and its Cd(II), Ce(III), and Th(IV) complexes

Comp. no.	ν_{as}(COO)	ν_s(COO)	Δ	ν(C=O) (–COOH)	ν(C=O) (amide)	ν(M–O) (COO)	ν(M–O) (H_2O)
IndoH	1590 sh	1454 sh	136	1716 sh	1685 sh	–	–
I	1590 s	1474 m	116	–	1680 sh	477 s	522 s
II	1589 m	1471 s	118	–	1681 sh	478 w, 432 s	599 s
III	1588 m	1471 sh	117	–	1682 sh	478 s, 433 w	547 s

Table 3. ^{1}H NMR spectral data of IndoH and its Cd(II) complex

Compound	δ, ppm of hydrogen				
	2H; $\underline{C}H_2$	3H; $\underline{C}H_3$	3H; $\underline{C}H_3O$	5H; $\underline{Ar}$H	H; COO$\underline{H}$
IndoH	2.10	3.50	4.10	6.15–7.15	11.00
Cd(II) complex	2.18	3.49	3.73	6.65–7.64	–

are listed in Table 2. No significant spectral changes are observed for IndoH after its coordination with the metal ions, expect for the frequencies related to the carboxylic (–COOH) groups [25]. The absence of the ν(O–H) and ν(C=O) absorption bands of the parent acid [3300 cm^{-1} and 1716 cm^{-1} of ν(O–H) and ν(C=O) bands for IndoH, respectively] in the IR spectra of the complexes is indicative of carboxylate group binding. The difference of bands of the prepared complexes; ν_{as}(COO) and ν_s(COO), is characterized for the carboxylate ligation. The ν_{as}(COO) and ν_s(COO) bands of Indo complexes are found at 1590–1588 and 1474–1471 cm^{-1}, respectively. The values for $\Delta[\nu_{as}(COO) - \nu_s(COO)]$ are in the range of 116–118 cm^{-1}, indicating that the coordination mode of the carboxylate ligand with the metal ion cores is monodentate [25–28]. Indomethacin complexes exhibited bands at the range of 3405–3444 cm^{-1}, attributed to the presence of coordinated and lattice water molecules [27]. The multiple weak bands at 478–432 cm^{-1} and the medium small bands at 599–522 cm^{-1} of the complexes are assigned to the $\nu(M–O)_{COO}$ and $\nu(M–O)_S$, respectively, where s is the oxygen bonded solvent (H_2O) [25, 27, 28].

^{1}H NMR spectra of IndoH and its Cd(II) complex. ^{1}H NMR spectra of IndoH and its Cd(II) complex are shown in Table 3 and Fig. 3; ^{1}H NMR data for free IndoH are: δ = 11.00 [H, COOH], 2.10 [2H, CH_2], 3.50 [3H, CH_3], 4.10 [3H, CH_3O], 6.15–7.15 [H, Ar–H]. ^{1}H NMR data for $[Cd(Indo)_2(H_2O)_2]\cdot H_2O$ solid complex are in agreement with coordination through the carboxylate group by the absence of the COOH signal in Cd(II) complex and the aromatic singals decreased in intensities, indicating that the magnetic environment of the aromatic ring has changed significantly with coordination. The signals observed at 2.48–2.50 and 3.36 ppm in case of Cd(II) complex, are assigned to the coordinated and uncoordinated water molecules. The results of elemental analyses, infrared and ^{1}H NMR spectral data are in agreement with each other to support the proposed structure of IndoH metal complexes.

Magnetic measurements of Ce(III) and Th(IV) complexes II and III. The magnetic moment value of the Th(IV) complex (**III**) was calculated from the

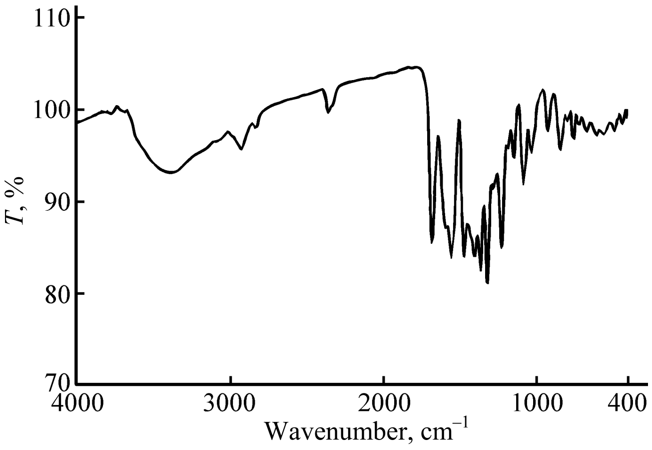

Fig. 2. FT–IR Spectrum of Ce(III) complex **II**.

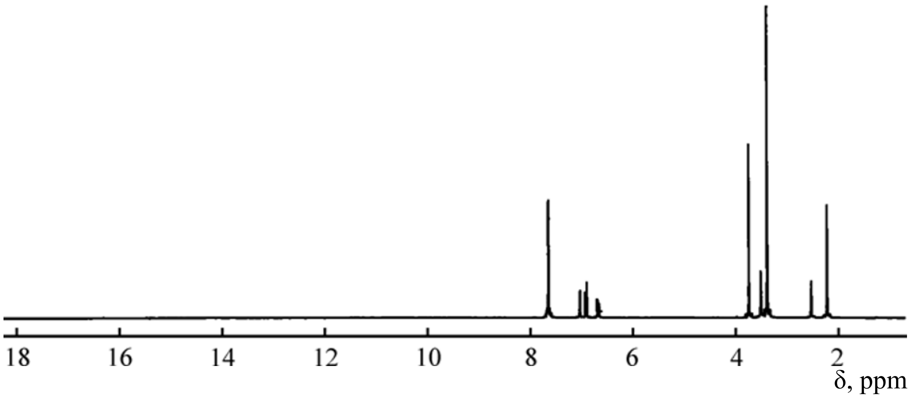

Fig. 3. ^{1}H NMR spectrum of Cd(II) complex **I**.

measured magnetic susceptibility after employing diamagnetic correction and revealed its diamagnetic nature as expected for thorium metal with 5F° configuration [29]. The magnetic moment of Ce(III) complex **II** lies at 2.58 BM and the magnetic moments values, μ_{eff} of the Ce(III) complexes are in the range 2.34–2.57 BM, being consistent with mono nuclear complexes and free from antiferromagnetism. The Ce(III) complex has a coordination number six and exists in octahedral geometry [30].

Electronic absorption spectra of Indo complexes. The formation of metal complexes was also confirmed by UV-Vis spectra. Fig. 4 shows as example the electronic absorption spectra of the Th(IV) complex **III** in 200–600 nm range. It can be seen that free IndoH has two distinct absorption bands. The first one at 275 nm may be attributed to π→π* transition of the hetero cyclic moiety and benzene ring. The second band observed at 350 nm is attributed to $n\rightarrow\pi^*$ electronic transition. In the spectra of the metal complexes,

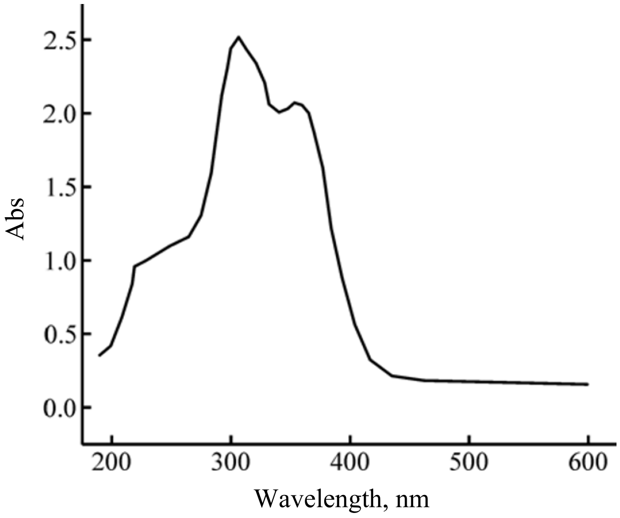

Fig. 4. Electronic absorption spectrum of Th(IV) complex **III.**

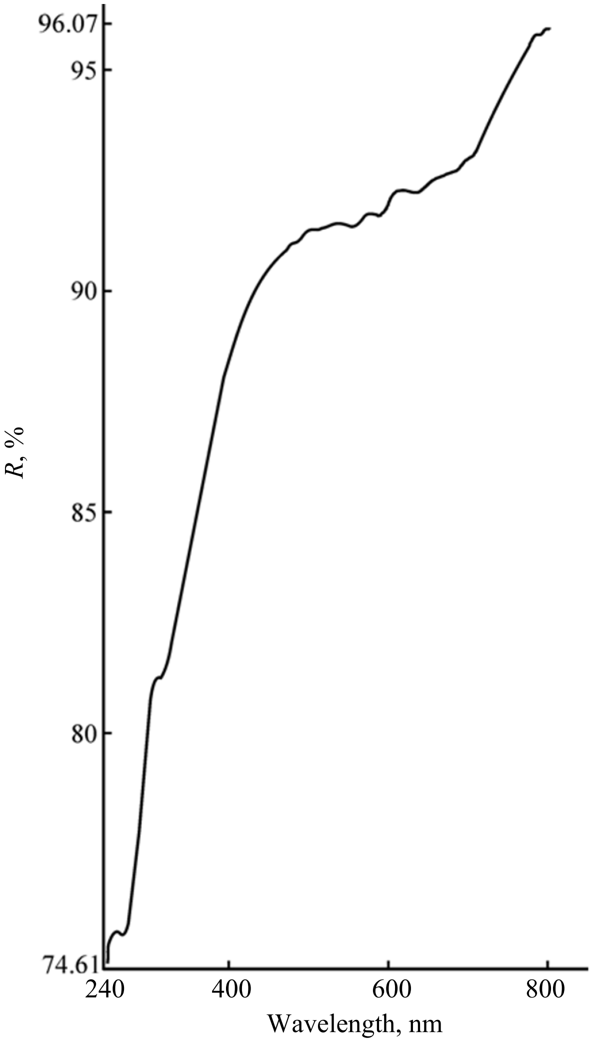

Fig. 5. Solid reflectance spectrum of Ce(III) complex **II**.

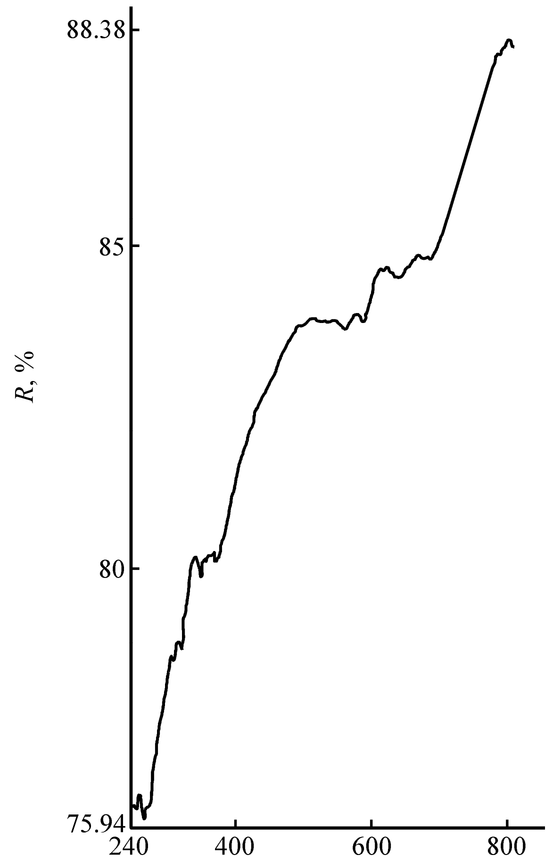

Fig. 6. Solid reflectance spectrum of Th(IV) complex **III**.

the two bands are bathochromically affected (Red-shifted), obviously suggesting the ligand has changed to the Zwitterionic form. The results clearly indicate that the ligand coordinate to metal ions via deprotonated carboxylate that in accordance with the results of the FTIR and ^{1}H NMR spectra.

The diffused reflectance spectrum of Ce(III) complex **II**, shown in Fig. 5 demonstrates two detectable absorption bands at 32258 and 38760 cm^{-1} which may be related to metal-ligand charge transfer (MLCT) excitations and corresponding to the octahedral geometry of the Ce(III) complex [29]. The solid reflectance spectrum of Th(IV) complex **III**, shown in Fig. 6 was recorded in the UV-Vis region. There are three detectable transitions at 39682, 32573, and 28248 cm^{-1} and ascribed to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and the charge transfer transition from the ligand to the metal, respectively [30].

Thermal analysis of Cd(II), Ce(III), and Th(IV) complexes. The data are listed in Table 4 and shown in Figs. 7 and 8. The weight losses for each chelate were calculated within the corresponding temperature ranges.

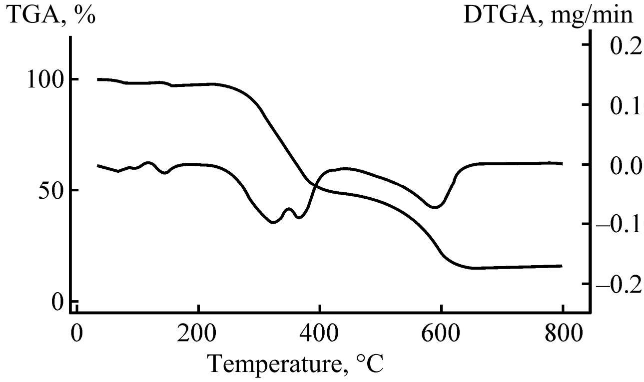

Fig. 7. TG/DTG curve of Cd(II) complex **I**.

[Cd(Indo)$_2$(H$_2$O)$_2$]·H$_2$O (I). The thermal decomposition of [Cd(Indo)$_2$(H$_2$O)$_2$]·H$_2$O complex occurs in three steps (Fig. 7). The first degradation step takes place in the range of 40–165°C and corresponds to the elimination of H_2O molecule with an observed weight loss of 2.83% (calculated 2.05%). The second step happens in the range of 165–420°C, assigned to the loss of 2 water molecules and $C_{21}H_{15}ClNO_5$ fragment with a weight loss of 49.22 (calculated 49.15%). The third decomposition step within the temperature range 420–640°C was accompanied by mass loss of 33.93% (calculated 34.15%), which is assigned to the loss of $C_{17}H_{15}ClNO_2$. The CdO is the final product remaining stable till 800°C. On the corresponding DTG curve, four peaks are observed. The first maximum is at 145°C and the second, third and fourth at 325, 369, and 594°C, respectively.

[Ce(Indo)$_3$(H$_2$O)$_3$] (II). The thermal decomposition of [Ce(Indo)$_3$(H$_2$O)$_3$] complex occurs completely

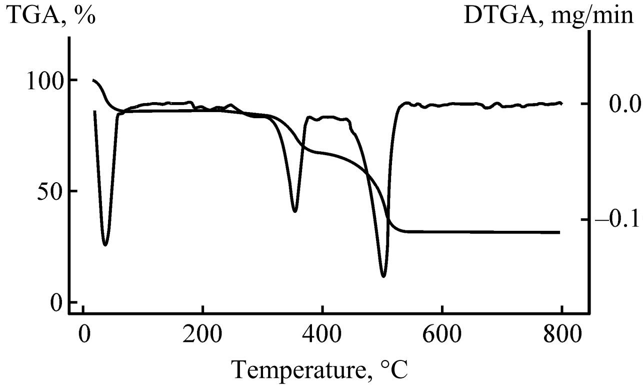

Fig. 8. TG/DTG curve of Th(IV) complex **III**.

Table 4. Thermal data for Indo complexes

Comp. no.	TG range, °C	DTG_{max}, °C	n^a	Mass loss, % found (calculated)	Total mass left	Assignment	Residue
I	40–165	145	1	2.83 (2.05)		Loss of H_2O.	CdO
	165–420	325, 369	1	49.22 (49.15)		Loss of $2H_2O$ and $C_{21}H_{15}ClNO_5$.	
	420–640	594	1	33.93 (34.15)	14.02 (14.65)	Loss of $C_{17}H_{15}ClNO_2$.	
II	225–670	459	1	67.56 (67.97)	32.44 (32.03)	Loss of $3H_2O$, $C_{37}H_{45}N_3Cl_3$ and 1/2 O_{21}	$1/2Ce_2O_3+20C$
III	20–80	36	1	13.97 (13.96)		Loss of $5H_2O$, Cl_2 and $2CO_2$.	ThO_2+23C
	215–365	353	1	17.50 (17.55)		Loss of $2H_2O$ and $C_{18}H_{15}NO_2$.	
	365–545	502	1	37.91 (38.23)	30.62 (30.26)	Loss of $C_{33}H_{45}Cl_2N_3O_8$.	

^{a} (*n*) is number of decomposition steps.

Table 5. Kinetic parameters using the Coats–Redfern (CR) and Horowitz–Metzger (HM) equations for Indo complexes

Comp. no.	Stage	Method	Parameter					*r*
			E^*, J mol^{-1}	A, s^{-1}	ΔS^*, J mol^{-1} K^{-1}	ΔH^*, J mol^{-1}	ΔG^* J mol^{-1}	
I	4	CR	1.47×10^5	7.10×10^6	-1.23×10^2	1.40×10^5	2.46×10^5	0.9959
		HM	1.75×10^5	2.82×10^8	-9.20×10^1	1.68×10^5	2.47×10^5	0.9987
II	1	CR	1.59×10^5	1.68×10^9	-7.58×10^1	1.53×10^5	2.08×10^5	0.9983
		HM	1.69×10^5	1.15×10^{10}	-5.98×10^1	1.63×10^5	2.07×10^5	0.9950
III	3	CR	2.93×10^5	9.27×10^{17}	-9.11×10^1	2.86×10^5	2.16×10^5	0.9963
		HM	3.10×10^5	1.21×10^{19}	-1.12×10^2	3.03×10^5	2.16×10^5	0.9965

in one step. This step proceeds at 225–670°C and corresponds to the loss of $3H_2O$, $C_{37}H_{45}N_3Cl_3$ and $1/2O_2$ molecules, representing a weight loss of 67.56% (calculated 67.97%). The final residue at the end of this stage is $1/2Ce_2O_3$ and 20C. From the corresponding DTG curve, only one peak is seen at 459°C.

$[Th(Indo)_4(H_2O)_2]\cdot5H_2O$ (III). The $[Th(Indo)_4(H_2O)_2]\cdot5H_2O$ complex decomposes in three steps (Fig. 8). The first step occurs at 20–80°C and corresponds to the loss of $5H_2O$, Cl_2 and $2CO_2$ molecules and representing a weight loss of 13.97% (calculated 13.96%). The second step occurs within the temperature range of 215–365°C, corresponding to the loss of $2H_2O$ and $C_{18}H_{15}NO_2$ fragment. Observed weight loss associated with this stage is 17.50% (calculated 17.55%). The third step takes place within the temperature range 365–545°C and can be assigned to the loss of $C_{33}H_{45}Cl_2N_3O_8$ molecule as CO, CO_2, NO, …, etc., gases and the mass loss due to this step was 37.91% (calculated 38.23%). The final residue at the end of this stage is ThO_2 and 23C. From the corresponding DTG curve, three peaks are noted. The first maximum is at 36°C, second and third peaks are found at 353 and 502°C, respectively.

Kinetic studies for Cd(II), Ce(III), and Th(IV) complexes of IndoH. In the present investigation, the general thermal behaviour of the Indo complexes in terms of stability ranges, peak temperatures and values of kinetic parameters [31, 32], are listed in Table 5 and shown in Figs. 9a (HM equation) and 9b (CR equation).

The thermodynamic data obtained with the two methods are in harmony with each other. The activation energies values of the Indo complexes reflect the thermal stability of the studied complexes. The thermograms and the calculated thermal parameters for the complexes show that the stability of these complexes depends on the nature of the central metal ion. It can be seen from the curves that the thermal stability of Th(IV) complex is higher than that for the corresponding Ce(III) and Cd(II) complexes with the same ligand. The thermal stability of the metal complexes was found to increase periodically with increase in atomic number of the metal and the larger value of charge/radius ratio [33].

The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.9950 to 0.9987, showing a good fit with linear function. It is clear that the thermal

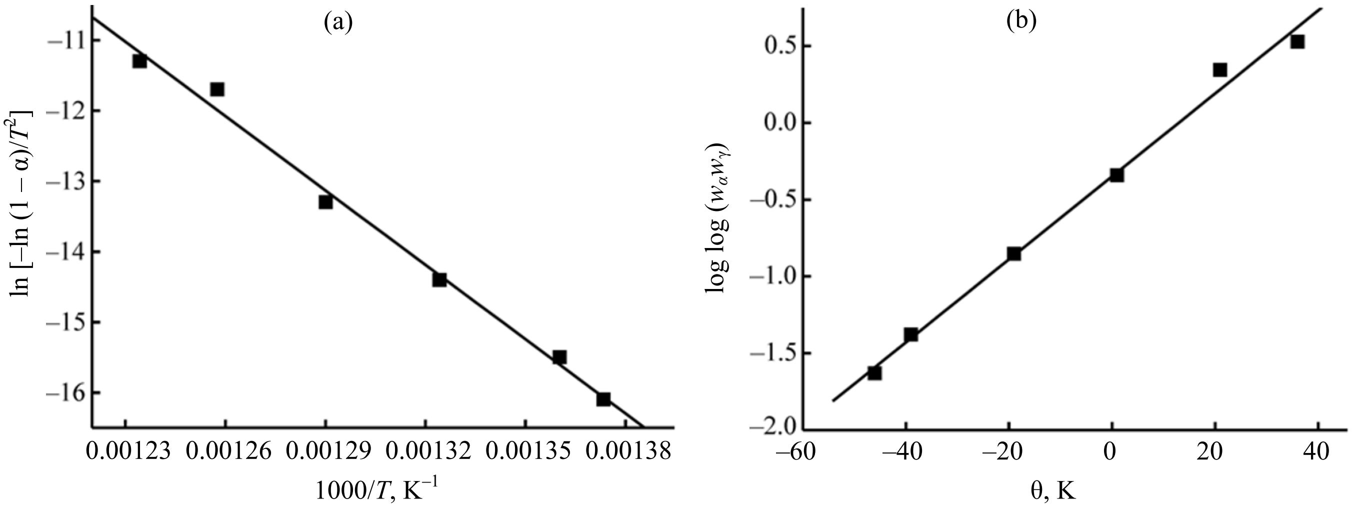

Fig. 9. Kinetic data curves for Th(IV) complex **III**. (a) HM equation and (b) CR equation.

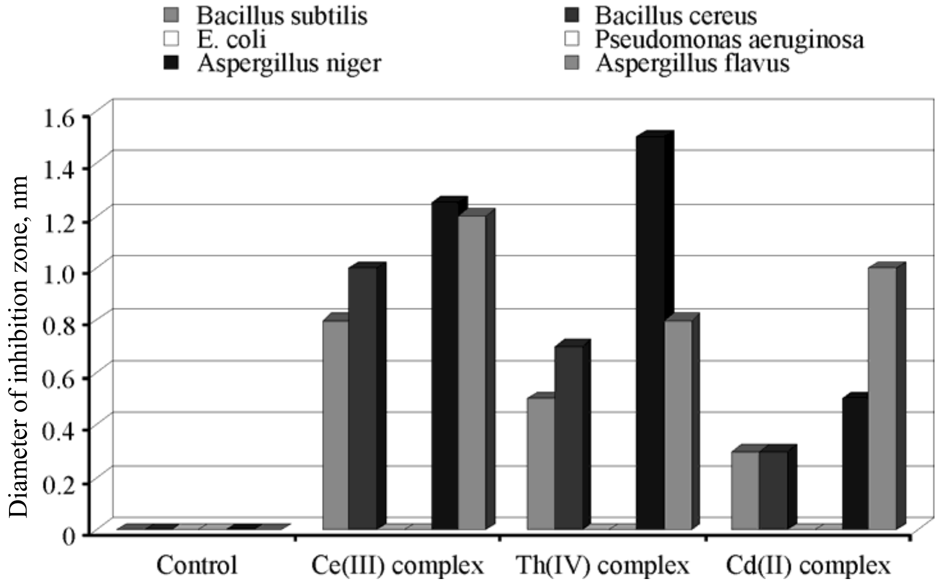

Fig. 10. Biological activity of Indo complexes.

decomposition process of all Indo complexes is non-spontaneous, i.e., the complexes are thermally stable.

Microbiological investigation of IndoH complexes. Obtained complexes were tested for antibacterial activities against Gram– (*E. coli* and *Pseudomonas aeruginosa*), Gram+ (*Bacillus subtilis* and *Bacillus cereus*) and antifungal such as *Aspergillus niger* and *Aspergillus flavus* organisms. Commercial DMSO was used to dissolve the tested samples. Concentration of each solution was 1.0×10^{-3} mol/L. The antimicrobial activity was estimated based on the size of inhibition zone. The complexes were found to have high activity against bacteria, especially Gram+ and two kinds of fungi, where the Th(IV) complex is more active than the Ce(III) and Cd(II) complexes against *Aspergllus niger*. The data are shown in Fig. 10.

Structure of IndoH complexes. The structures of the complexes of Indo with Cd(II), Ce(III), and Th(IV) ions have been confirmed by the elemental analyses, IR, molar conductance, UV-Vis and thermal analysis data. Thus, from the IR spectra, it is concluded that IndoH behaves as a monobasic monodentate ligand coordinated to the metal ions via the deprotonated

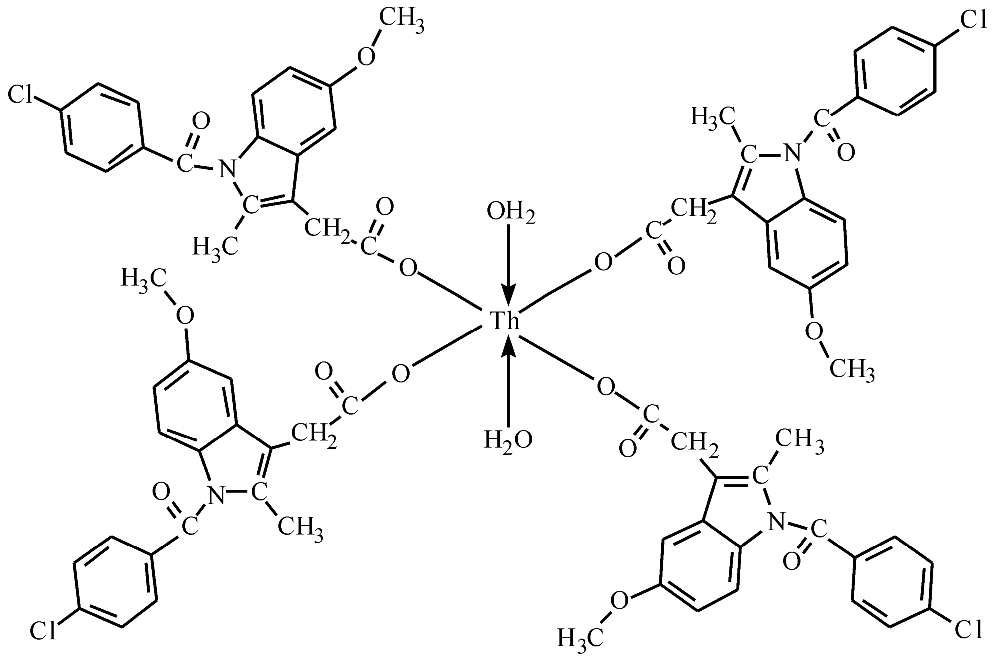

Fig. 11. Structure of Th(IV) complex **III**.

carboxylate O atom. From the molar conductance data, it is found that the complexes are non-electrolytes. Because of the above observations, tetrahedral and octahedral geometries are suggested for the investigated complexes. As an example, the proposed structure of Th(IV) complex **III** is shown in Fig. 11.

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