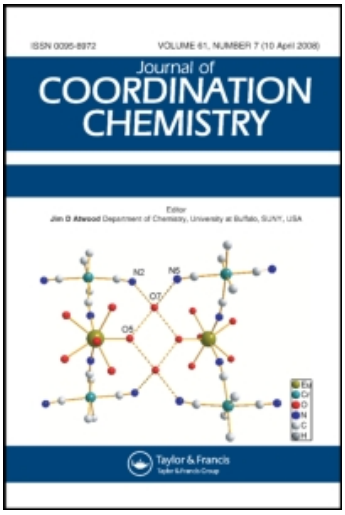

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Complexation and thermogravimetric investigation on tin(II) and tin(IV) with norfloxacin as antibacterial agent

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Complexation and thermogravimetric investigation on tin(II) and tin(IV) with norfloxacin as antibacterial agent

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The interaction of tin(II) and tin(IV) chlorides with norfloxacin (NOR) has been investigated. Elemental analysis, infrared, mass spectra and thermal analysis have been used to characterize the isolated solid complexes. The results support the formation of complexes with the formula $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ and $[Sn(NOR)_3]Cl_4$. The infrared spectra of the isolated solid complexes suggested that NOR act as bidentate ligand through the carbonyl oxygen atom and one oxygen atom of the carboxylic group forming six-membered rings with the tin ions. The interpretation, mathematical analysis and evaluation of kinetic parameters of thermogravimetric (TGA) and its differential (DTG), such as entropy of activation, pre-exponential factors, activation energy evaluated by using Coats–Redfern and Horowitz–Metzger equations are carried out for two complexes. The data obtained indicate that the two complexes decompose in one stage and general mechanisms describing the decomposition are suggested. Furthermore, the electronic, and ^{1}H NMR spectra have been studied.

Keywords: Tin chlorides; Norfloxacin; Thermal analysis; ^{1}H NMR spectra

1. Introduction

Norfloxacin (NOR) is a quinolone antibacterial agent used in the treatment of a wide range of infections. Quinolone antibiotics are potentially capable of forming coordinate bonds with many metal ions via the carbonyl oxygen and carboxylic acid groups [1–5]. These studies indicate that coordination of quinolones to metal ions such as Mg(II) and Ca(II) are important for activity of the quinolone antibiotic and on their absorption [6–11].

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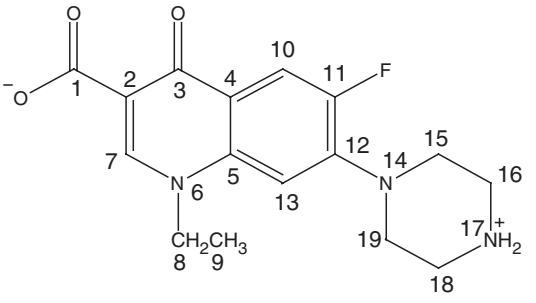

Figure 1. Numbering scheme of norfloxacin.

Chen *et al.* [12] reported the synthesis of two dimeric complexes of norfloxacin with magnesium and calcium(II) chlorides. The crystal structures of these complexes, and all solids isolated from the neutral quinolones in the Zwitterionic state (figure 1), showed that the carbonyl oxygen and one oxygen of the carboxylate group of the norfloxacin ligand are directly bonded to the metal ions [13–18].

In previous studies [19, 20] the interaction of NOR with alkaline earth metal ions and the biologically activity of the complexes formed from this interaction have been examined. The present study deals with the preparation, the chemical and spectroscopic characterization, the thermal analysis and molecular structures of the solid complexes formed from the interaction of NOR with Sn(II) and Sn(IV) chlorides in acetone and methylene chloride, respectively.

2. Experimental

$SnCl_2$ and $SnCl_4$ were obtained from Aldrich Chemical Co., while norfloxacin was obtained from Merck Chemical Co.

2.1. *Preparation and characterization of the complexes*

The yellowish solid complex of Sn(II)–NOR was prepared by the addition of 0.224 g (1 mmol) of $SnCl_2 \cdot 2H_2O$ in 50 mL acetone to 0.638 g (2 mmol) of NOR suspended in 40 mL of acetone. The reaction mixture was stirred for 15 h at room temperature. After that, the volume of the reaction mixture was reduced and the precipitated complex was filtered off and washed several times with acetone and dried under vacuum over calcium chloride. The pale yellow solid complex of Sn(IV)–NOR was prepared by the addition of 0.26 g (1 mmol) of tin tetrachloride (1 mL of 1 M $SnCl_4$ dissolved in methylene chloride) to 0.957 g (3 mmol) of NOR suspended in CH_2Cl_2. The reaction mixture was stirred for 12 h at room temperature. The precipitated complex was then filtered off, washed several times with methylene chloride and then dried under vacuum over calcium chloride.

Carbon, hydrogen, nitrogen and halogen contents in the obtained solid products were determined by elemental analysis using a Perkin Elmer CHN 2400. Tin content was determined by using atomic absorption and also gravimetrically as tin oxides. The atomic absorption spectrometer PYE-UNICAM SP 1900 fitted with a tin lamp

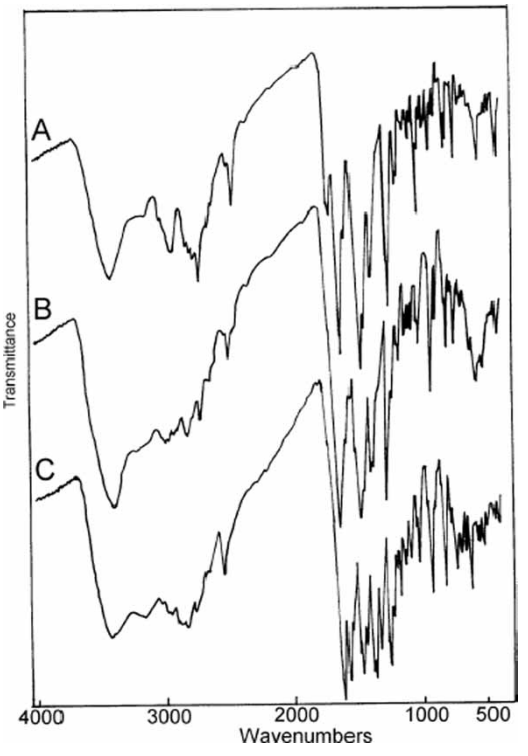

Figure 2. Infrared spectra of (A) (NOR); (B) $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ and (C) $[Sn(NOR)_3]Cl_4$ complexes.

was used for this purpose. Analysis of the products obtained: $[Sn(C_{16}H_{18}N_3O_3F)_2]Cl_2 \cdot 4H_2O$ (899.69): C; 42.38 (42.68); H; 4.86 (4.89); N; 9.31 (9.33); Cl; 7.85 (7.89); Sn; 13.15 (13.19), $[Sn(C_{16}H_{18}N_3O_3F)_3]Cl_4$ (1217.69): C; 46.57 (46.61); H; 4.41 (4.43); N; 10.31 (10.34); Cl; 11.61 (11.66); Sn; 9.72 (9.74).

The infrared spectra of the two solid complexes and norfloxacin were recorded using a Genesis II FT-IR Spectrometer as potassium bromide discs. Thermogravimetric (TG) and differential (DTG) thermogravimetric analysis were carried out under N_2 using detectors model Shimadzu TGA-50H. The electronic spectra of norfloxacin and the two complexes in dimethyl sulphoxide were recorded in the region of 700–200 nm using a Shimadzu UV-Spectrophotometer model 1601 PC with a 1 cm quartz cell. ^{1}H NMR measurements were made on a Varian Gemini 200 MHz. The mass spectra were determined at 70 eV by using an AEI MS 30 mass spectrometer on solid samples.

3. Results and discussion

Norfloxacins of Sn(II) and Sn(IV) were prepared as solids with a molar ratio of 1:2 and 1:3, respectively. The infrared spectra of $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ and $[Sn(NOR)_3]Cl_4$ complexes are similar, figure 2, showing a sharp broad absorption near 3400 cm^{-1} and a group of bands with different intensity at 2848, 2827, 2480

and 2472 cm^{-1}, figure 2. These bands can be assigned to the vibration of the quaternized nitrogen of the piperazinyl group which indicates the zwitterionic form of NOR is involved in coordination to tin [21]. The IR spectrum of Sn(II) complex shows an absorption band at 3430 cm^{-1}, table 1. This band is not observed in the spectra of free norfloxacin or tin(IV) complex and is attributed to lattice water. This suggestion was also supported by thermal analysis.

The bands observed at 1727, 1716 and 1630 cm^{-1} in the spectrum of the free NOR have been assigned before to the stretching vibration of the carboxylic ν(COOH) and the carbonyl groups ν(C=O), respectively [22–25]. The absence of the $\nu(COO^-)$ bands at 1727 and 1716 cm^{-1} in the two complexes indicates coordination. The asymmetric stretching carboxylate bands appears at 1632 and 1630 cm^{-1} for the Sn(II) and Sn(IV) complexes, respectively. The spectra of the two complexes also show medium or strong intensity bands at 1400, 1388 and 1385 cm^{-1}. These bands are absent in the spectrum of NOR and most likely due to the symmetric vibration of the ligated COO^- group. However, the peak observed at 1595 cm^{-1} in the IR spectrum of NOR which contains a protonated carboxyl group indicates that assignment of this band to the asymmetric stretch $\nu_{as}(COO^-)$ of carboxyl group is doubtful [26].

The carboxylato group can act as a unidentate, bidentate or bridging ligand and distinction between these binding states can be made from the frequency separation $[\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)]$ between the symmetric and asymmetric stretching of this group [27, 28]. Unidentate carboxylato complexes exhibit $\Delta\nu$ values around 200 cm^{-1} and for bidentate or chelating carboxylato complexes $\Delta\nu$ is smaller than ionic value ($\Delta\nu < 100\ cm^{-1}$); bridging complexes show $\Delta\nu$ around 150 cm^{-1}. The observed $\Delta\nu$ for the Sn(II) and Sn(IV) NOR complexes are around 200 cm^{-1}, table 1, suggesting a unidentate interaction of the carboxylate group.

The ν(CO) in the spectrum of NOR is at 1620 cm^{-1} as a shoulder. In the spectra of Sn(II) and Sn(IV) NOR complexes, the ν(CO) is slightly effected by the interaction with tin ions and appear at 1617 or 1618 cm^{-1}. Similar behavior has been observed in several quinolone-metal ion complexes [24, 25]. The coordination of metal ions via carboxylate is confirmed by the ν(M–O) bands at 658, 625 and 548 cm^{-1} for Sn(II) and at 623, 565 and 548 cm^{-1} for Sn(IV).

Accordingly, the NOR acts as a bidentate ligand through the oxygen atom of the carbonyl group and one of the oxygen atoms of the carboxylate group. The infrared spectra of the prepared complexes display changes in the aromatic ring vibrations in comparison to the corresponding absorption bands of free NOR, table 1.

The electronic spectra of the norfloxacin along with the Sn(II) and Sn(IV) complexes in DMSO are shown (figure 3). The free norfloxacin absorbed at 265, 285 and 334 nm, while the absorption spectra for Sn(II) (300, 338 nm) and Sn(IV)-NOR (289, 338 nm) complexes do not show the band at 265 nm. This shift of λ_{max} to higher values (bathochromic shift) may be due to conjugation or attachment to the auxochrome in the two norfloxacin complexes.

Thermal stabilities of norfloxacin and $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ or $[Sn(NOR)_3]Cl_4$ were studied using thermogravimetric (TG) and differential thermogravimetric (DTG) analysis under N_2 flow, figure 4. From the thermal curves, data on thermal decomposition of the prepared complexes were obtained. Norfloxacin is thermally stable in the temperature range 25–56°C. Decomposition of the NOR started at 59°C and finished at 726°C with two stages. The first stage of decomposition occurs in the range 59–188°C with a maximum at 116°C accompanied by a weight loss of 8.74%,

Table 1. Infrared frequencies[a] (cm^{-1}) and tentative assignments[b] for norfloxacin (NOR) as a ligand; $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ and $[Sn(NOR)_3]Cl_4$ complexes.

NOR	$[Sn(NOR)_2]Cl_2 \cdot 4H_2O$	$[Sn(NOR)_3]Cl_4$	Assignments
–	3430 m,br	–	ν(O–H); H_2O
3399 ms	3398 w	3400 m	ν(N–H)
3267 vw, 3228 vw, 3189 vw	3213 vw, 3199 vw, 2996 w	3189 vw, 3174 vw, 3031 w	ν(C–H) $\nu(-NH_2^+)$
3130 vw, 3021 w, 2927 m	2971 w, 2923 w, 2827 m, 2723 m, 2667 w, 2560 vw	2969 w, 2915 w, 2848 w	
2823 w, 2796 w, 2764 w	2510 m, 2472 sh	2773 w, 2678 vw, 2553 m	
2723 m, 2696 vw, 2654 w		2480 sh	
2617 w, 2511 w, 2468 m			
1727 sh, 1716 ms	–	–	ν(C=O): (OCO^-)
–	1632 vs	1630 sh	$\nu_{as}(COO^-)$
1630 vs, 1620 sh	1617 sh	1618 vs	ν(C=O)
1595 w, 1552 w	1585 w, 1558 w 1520 w	1583 s, 1558 w, 1538 vw, 1504 m	Phenyl breathing modes
1482 vs, 1454 m	1481 s, 1454 w	1485 ms, 1456 ms	CH; deformation of $-CH_2-$
1396 s	1400 m, 1388 m	1400 s, 1385 s	$\nu_s(COO^-)$
1307 vw	1368 sh, 1355 sh, 1343 sh	1348 s	$\delta_b(CH_2)$
1277 vw, 1263 s, 1248 vw	1276 vs, 1240 w, 1219 vw	1285 sh, 1268 s, 1240 m	ν(C–C)
1201 m	1192 m	1207 m	ν(C–O)
1192 m	1142 m	1180 ms	ν(C–N)
1153 vw, 1142 w, 1132 w	1115 m, 1088 m, 1045 vw	1139 m, 1126 w, 1103 w	$\delta_r(CH_2)$
1115 w, 1095 m, 1076 m	1036 m, 964 w, 933 s	1093 w, 1047 m, 1033 s	
1051 vw, 1036 ms, 1024 w		962 w, 933 s	
1005 m, 982 m			
972 w, 935 ms, 916 m 899 m, 887 m, 858 w	898 ms, 827 w, 819 w, 810 ms, 787 w, 769 w	902 w, 850 vw, 827 s, 812 sh, 785 m, 769 m	CH– bend; phenyl
823 ms, 804 ms			
750 s, 706 m	752 ms, 712 vw	736 s, 702 m	$\delta_b(COO^-)$
667 w, 631 w,br, 569 ms	698 w, 658 w, 625 m, 567 m, 548 vw, 523 m	660 m, 623 ms, 565 m, 548 m, 520 m, 497 m	ν(Sn–O) ring deformation
524 w, 499 m, 474 m 453 vw, 430 ms	499 vw, 474 w, 453 vw, 420 m	445 m, 420 m	

[a] s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad; [b] ν, stretching; δ, bending.

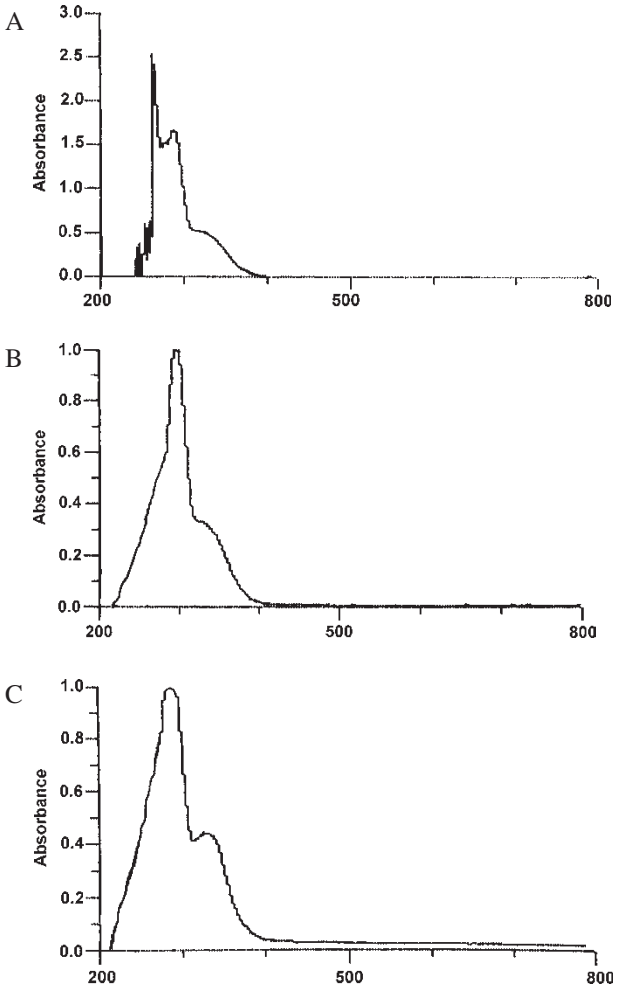

Figure 3. Electronic absorption spectra of (A): NOR ligand in DMSO. (B): $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ complex in DMSO. (C): $[Sn(NOR)_3]Cl_4$ complex in DMSO.

corresponding exactly to the loss of ethylene molecule (C_2H_4). The second stage of decomposition occur at three maxima 330, 423 and 654°C with the total weight loss accompanying these steps was 83.73%, and may be attributed to the loss of $6C_2H_2 + 3NO + HF + 1/2H_2$, in reasonable agreement with the theoretical value of 83.69%, giving two carbon atoms as the final decomposition product. The tin complexes are stable up to 230°C and then are decomposed in one step at two maxima to the corresponding tin oxides at 250–730°C range for Sn(II) complex and 250–780°C for Sn(IV) complex range with intermediate formation of very unstable products which were not identified. For hydrated Sn(II) norfloxacin the stage of decomposition occurs at a maximum temperatures 311.5 and 640.6°C and is accompanied by a weight loss of 75.03%, associated with the loss of $8C_2H_2 + 2C_2H_4 + 4CO + 5H_2O + 2NH_3 + 2N_2 + 2HCl + 2HF$. The actual weight loss from this stage is very close to calculated (74.35%). The loss of four water molecules at relatively

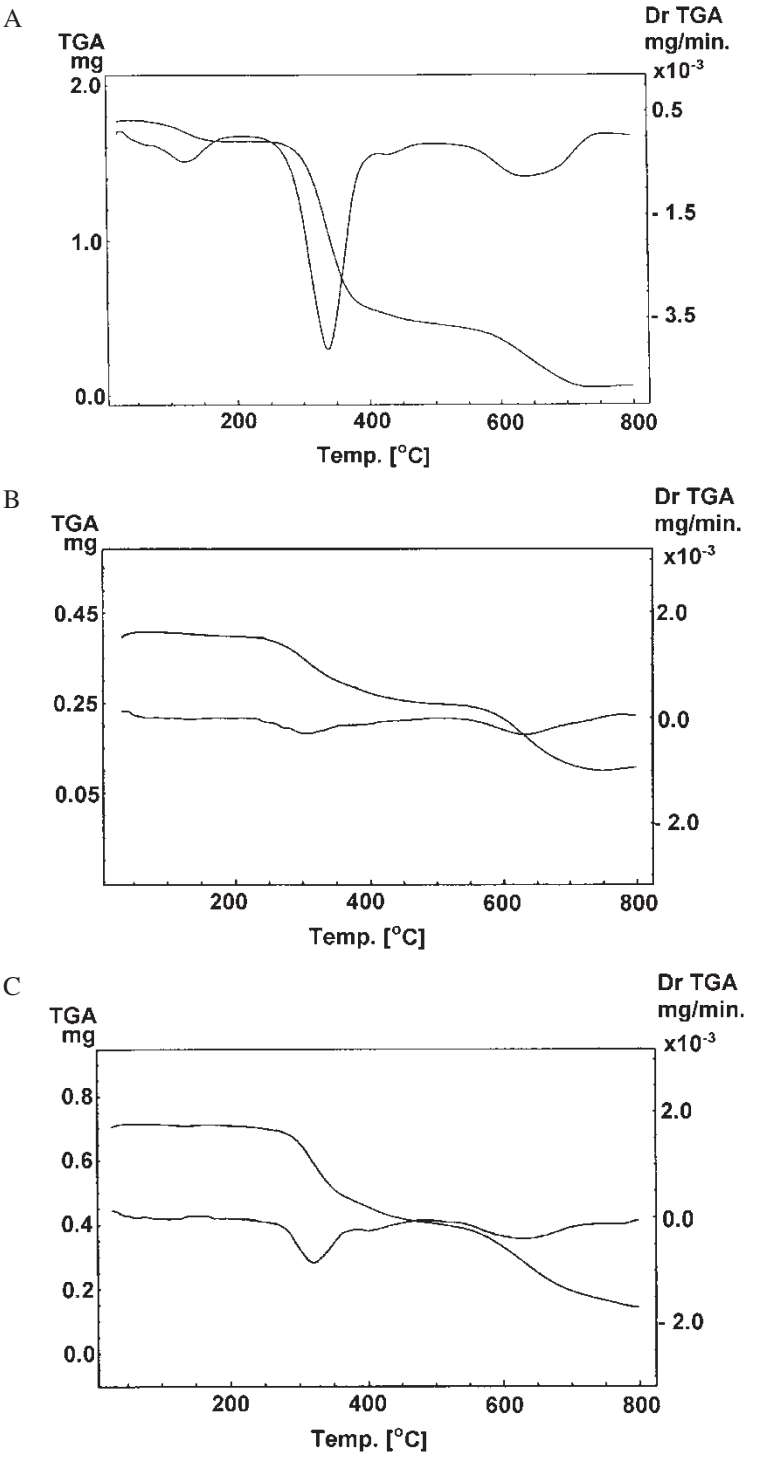

Figure 4. TGA and DTG diagrams of: (A): NOR ligand. (B): $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ complex. (C): $[Sn(NOR)_3]Cl_4$ complex.

Sn(II)-NOR complex

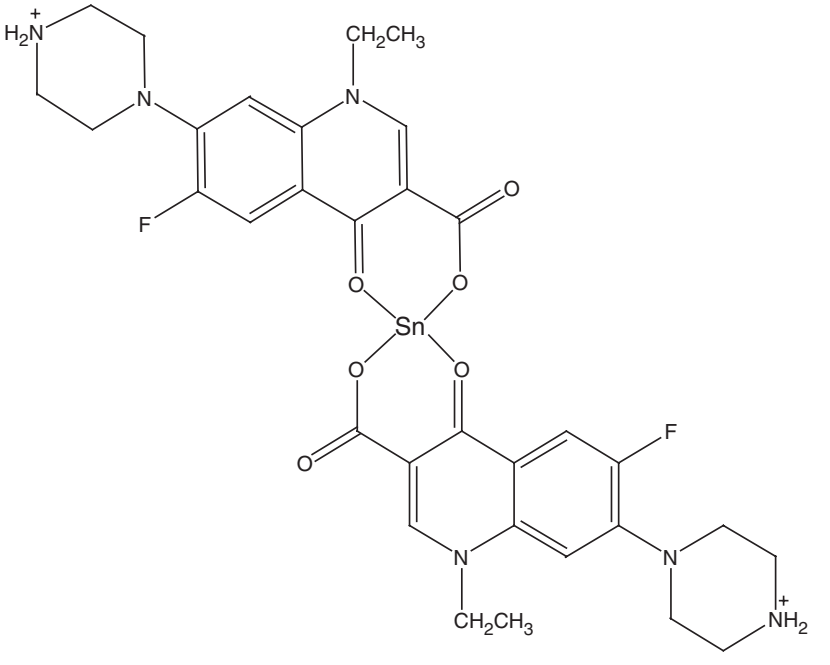

Figure 5. The coordination mode of Sn(II) and Sn(IV) with norfloxacin.

high temperature may indicate that these water molecules undergo strong H-bonding. For the Sn(IV)-norfloxacin complex the two maxima are 325 and 634.6°C and the weight loss found is equal to 78.06%, corresponding to the loss of $16C_2H_2 + 3C_2H_4 + 5NO + 2H_2O + 1/2Cl_2 + 2N_2 + 3HCl + 3HF$ agreeing quite well with the calculated value 77.82%, and the tin oxides is the expected residue up to 800°C. The proposed structural formula, based of the results discussed in our article, is shown in figure 5.

The infrared spectra of the final products of the thermal analysis show the absence of all bands associated with the norfloxacin and water only the characteristic spectra for tin oxides, SnO and SnO_2.

Accordingly, the following mechanisms are proposed for the thermal decomposition of tin norfloxacin complexes:

$$(1)\quad C_{16}H_{18}N_3O_3F \xrightarrow{116^\circ C} C_2H_4 + C_{14}H_{14}N_3O_3F$$

$$C_{14}H_{14}N_3O_3F \xrightarrow{330^\circ C,\ 423^\circ C,\ 654^\circ C} 2C + 6C_2H_2 + 3NO + HF + 1/2H_2$$

$$(2)\quad [Sn(C_{16}H_{18}N_3O_3F)_2]Cl_2 \cdot 4H_2O \xrightarrow{311.5^\circ C,\ 640.6^\circ C}$$

$$SnO + 8C + 8C_2H_2 + 2C_2H_4 + 4CO + 5H_2O + 2NH_3 + 2N_2 + 2HCl + 2HF$$

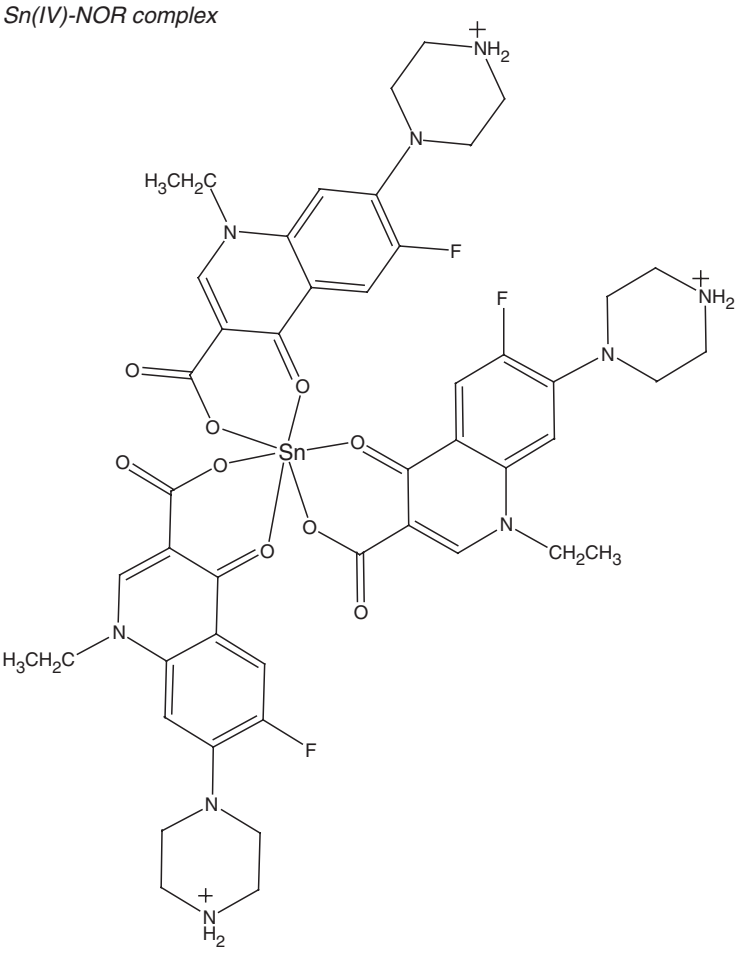

Figure 5. Continued.

(3) $[Sn(C_{16}H_{18}N_3O_3F)_3]Cl_4 \xrightarrow{325^\circ C,\ 634.6^\circ C}$

$$SnO_2 + 10C + 16C_2H_2 + 3C_2H_4 + 5NO + 2H_2O + 1/2Cl_2 + 2N_2 + 3HCl + 3HF$$

There has been increasing interest in determining rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves. Several equations [29–36] have been proposed to analyze a TG curve and obtain values for kinetic parameters. Many authors [29–33] have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion [30], using

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the fraction decomposed at time t, $k(T)$ is the temperature dependent function and $f(\alpha)$ is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function $k(T)$ is of the Arrhenius type and can be considered as the rate constant k.

$$k = Ae^{-E^*/RT} \tag{2}$$

where R is the gas constant in ($J\,mol^{-1}\,K^{-1}$). Substituting equation (2) into equation (1), we get,

$$\frac{d\alpha}{dt} = \left(\frac{A}{\varphi\, e^{-E^*/RT}}\right) f(\alpha) \tag{3}$$

where ϕ is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form,

$$\ln g(\alpha) = \frac{-E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right] \tag{4}$$

where $g(\alpha)$ is a function of α dependent on the mechanism of the reaction. The integral on the right hand side is known as temperature integral and has no solution. Several techniques have been used for the evaluation of the temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll [29] integral method of Coats and Redfern [31], the approximation method of Horowitz and Metzger [34].

In the present investigation the general thermal behavior of the norfloxacin ligand and the two complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in figure 6 and table 2. The kinetic parameters have been evaluated using the following methods and the results obtained by these methods are compared with one another. The following two methods are briefly discussed.

3.1. *Coats–Redfern equation*

The Coats–Redfern equation (5), which is a typical integral method, can be represented as:

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\varphi}\int_{T_1}^{T_2} \exp\left(\frac{-E^*}{RT}\right) dt \tag{5}$$

For convenience of integration, the lower limit T_1 is usually taken as zero. This equation on integration gives:

$$\ln\left[-\ln\frac{(1-\alpha)}{T^2}\right] = \frac{-E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right] \tag{6}$$

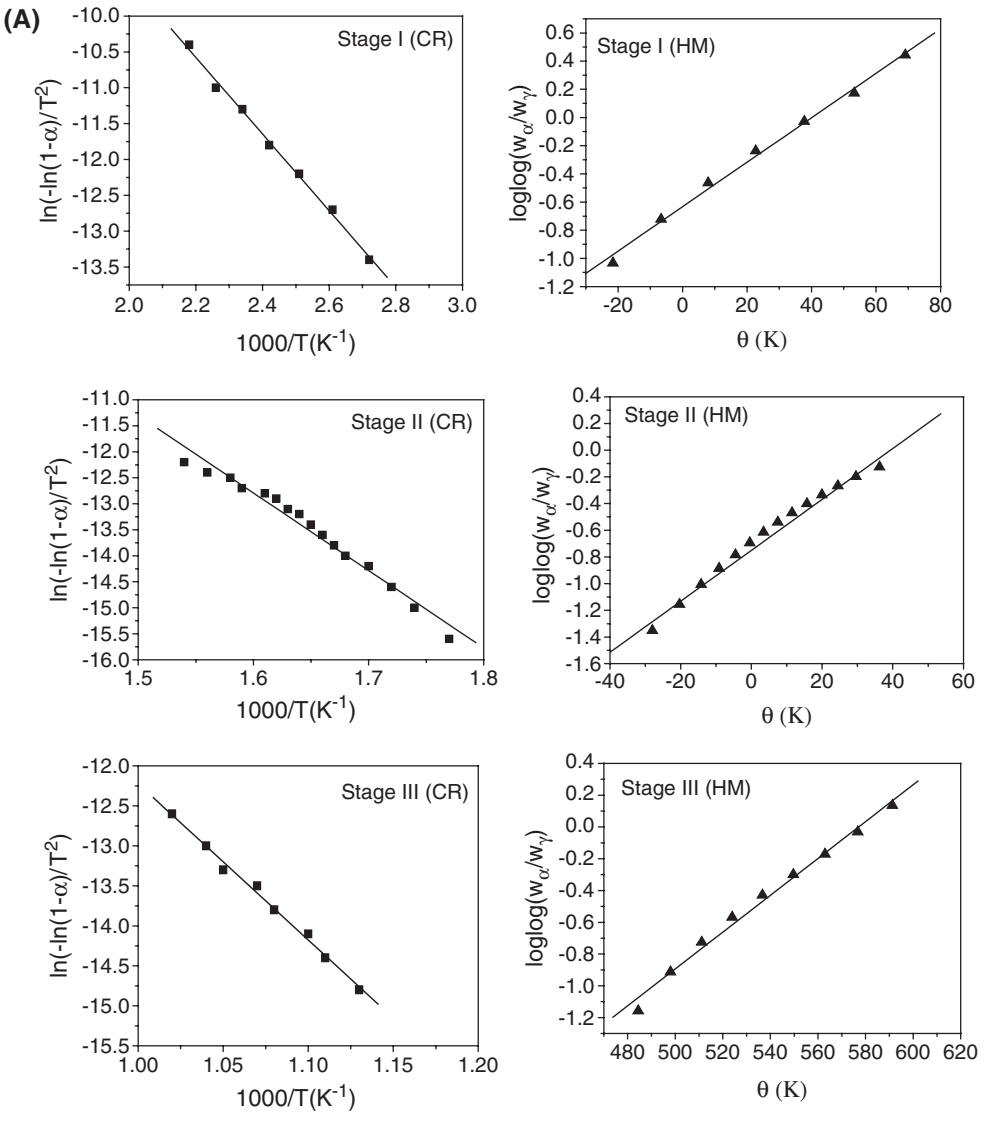

Figure 6. Coats–Redfern (CR) and Horowitz–Metzger (HM) plots for (A): norfloxacin; (B): $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$; (C): $[Sn(NOR)_3]Cl_4$.

A plot of left-hand side (LHS) against $1/T$ was drawn. E^* is the energy of activation in kJ mol^{-1} and calculated from the slope and A in (s^{-1}) from the intercept. The entropy of activation ΔS^* in (J K^{-1} mol^{-1}) was calculated by using equation (7):

$$\Delta S^* = R \ln\left(\frac{Ah}{k_B T_s}\right) \tag{7}$$

where k_B is the Boltzmann constant, h is Plank's constant and T_s is the DTG peak temperature [37].

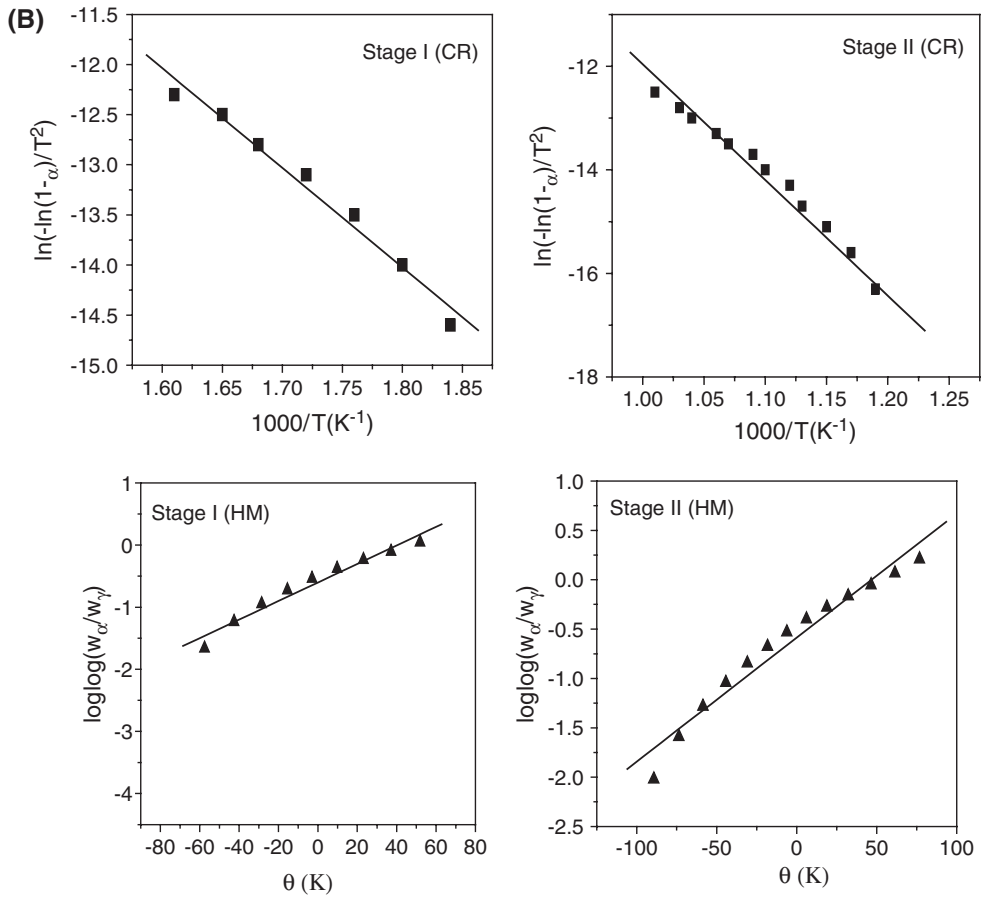

Figure 6. Continued.

3.2. *Horowitz–Metzger equation*

The Horowitz–Metzger equation is illustrative of the approximation methods. These authors derived the relation:

$$\log\left[\frac{\{1-(1-\alpha)^{1-n}\}}{(1-n)}\right] = \frac{E^*\theta}{2.303RT_s^2} \quad \text{for } n \neq 1 \tag{8}$$

when $n = 1$, the LHS of equation (4) would be $\log[-\log(1-\alpha)]$. For a first-order kinetic process the Horowitz–Metzger equation (9) may be written in the form:

$$\log\left[\log\left(\frac{w_\alpha}{w_\gamma}\right)\right] = \frac{E^*\theta}{2.303RT_s^2} - \log 2.303 \tag{9}$$

where $\theta = T - T_s$, $w_\gamma = w_\alpha - w$, $w_\alpha =$ mass loss at the completion of the reaction; $w =$ mass loss up to time t. The plot of $\log[\log(w_\alpha/w_\gamma)]$ versus θ was drawn and found

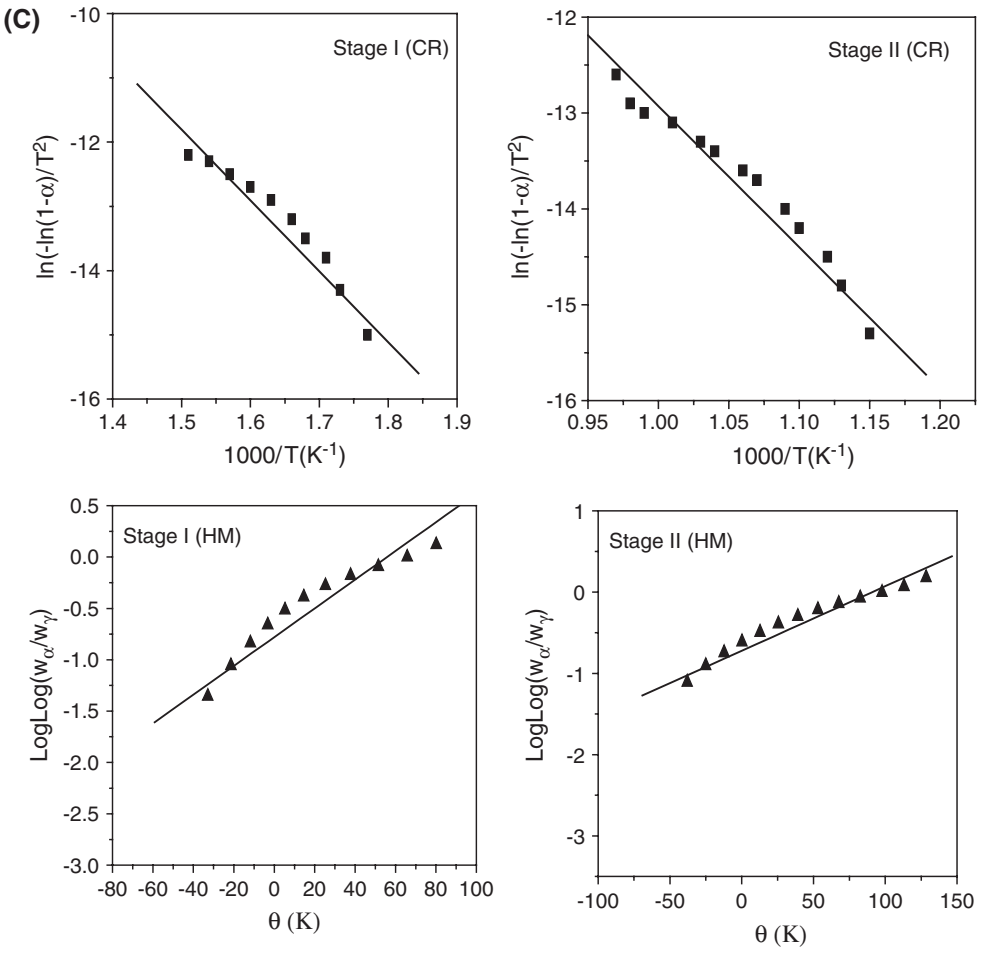

Figure 6. Continued.

to be linear from which the slope E^* was calculated. The pre-exponential factor, A, was calculated from equation (10):

$$\frac{E^*}{RT_s^2} = \frac{A}{[\varphi \exp(-E^*/RT_s)]} \tag{10}$$

The entropy of activation, ΔS^*, was calculated from equation (3). The enthalpy of activation, ΔH^*, and Gibbs free energy, ΔG^*, were calculated from;

$$\Delta H^* = E^* - RT \tag{11}$$

and

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{12}$$

Table 2. Kinetic parameters determined using the Coats–Redfern (CR) and Horowitz–Metzger (HM).

Compound	Decomposition range/K	T_s/K	Method	E^*/kJ mol^{-1}	A/s^{-1}	ΔS^*/J K^{-1} mol^{-1}	ΔH^*/kJ mol^{-1}	ΔG^*/kJ mol^{-1}	R
NOR	336–458	389	CR	44.3	4.24×10^3	−178	41.1	110	0.9975
			HM	45.8	1.26×10^4	−169	42.5	108	0.9973
	537–735	603	CR	126.0	1.21×10^3	−173	121.0	225	0.9906
			HM	133.0	3.61×10^9	−68	128.0	169	0.9863
	844–996	927	CR	175.0	1.67×10^4	−174	167.0	328	0.9945
			HM	191.0	3.82×10^8	−90	183.0	267	0.9948
$[Sn(NOR)_2]Cl_2 \cdot 4H_2O$	511–651	584	CR	97.8	3.29×10^6	−126	92.9	166	0.9907
			HM	113.2	1.30×10^8	−95	108.3	164	0.9852
	808–1006	913	CR	207.0	3.90×10^9	−71	200.0	264	0.9852
			HM	222.0	1.30×10^8	−98	214.0	305	0.9808
$[Sn(NOR)_3]Cl_4$	536–692	598	CR	128.0	8.64×10^8	−79	123.0	171	0.9875
			HM	144.0	4.96×10^{10}	−46	139.0	167	0.9835
	843–1051	907	CR	174.0	1.17×10^9	−80	166.0	239	0.9780
			HM	189.0	4.96×10^{10}	−49	181.0	226	0.9783

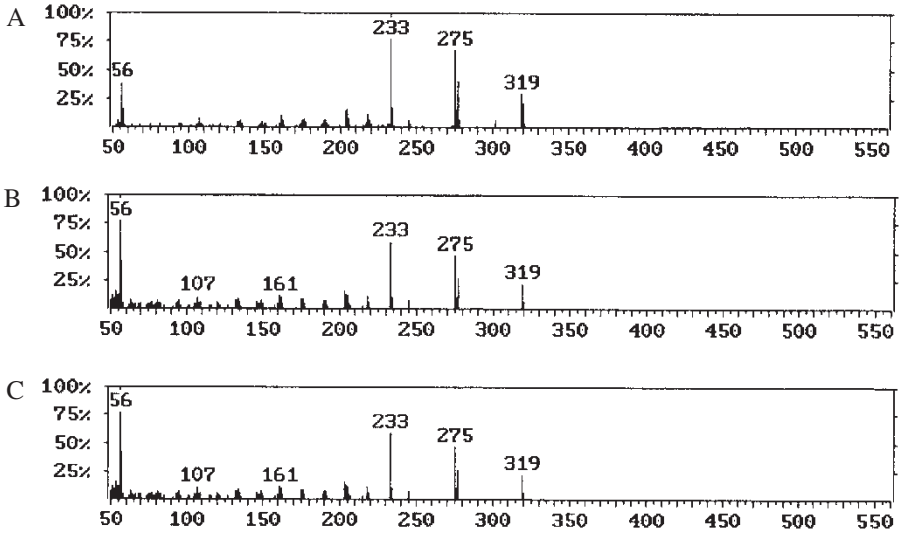

Figure 7. Mass spectra diagrams of: (A): NOR ligand in. (B): $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ complex. (C): $[Sn(NOR)_3]Cl_4$ complex.

The kinetic parameters, E^*, ΔH^*, ΔS^* and ΔG^* calculated with Coats–Redfern and Horowitz–Metzger equations, are tabulated in table 2. Taking the first decomposition range about (500–700°C) as a criterion, the data show that activation energy, E^*, activation enthalpy, ΔH^*, activation entropy, ΔS^*, and Gibbs free energy, ΔG^*, for Sn(IV)–NOR complex are higher than those for Sn(II)-complex, showing that the thermal stability for the Sn(IV) complex is higher than for the Sn(II) complex, behavior which can be explained on the basis of the oxidation state of tin and the number of attached ligands. By comparison, the values of the activation entropies, ΔS^* in these two complexes and the free norfloxacin ligand indicate that the activated complex has a more ordered structure than the reactants.

The fragmentation patterns of our studied complexes beside the norfloxacin ligand were obtained from the mass spectra, presented in figure 7. When we make a comparison between norfloxacin as a ligand and both tin–NOR complexes, the line at M. wt. = 319 corresponds to molecular ion (M. wt. of NOR ligand) is a cofactor peak in the two complexes. The other three main parts in the NOR ligand or Sn(II)–NOR and Sn(IV)–NOR complexes appear at the positions: $m/z = 275$, 233 and finally at 56 with variable abundance. These lines correspond to the fragments $[C_{15}H_{18}N_3OF]^+$, $[C_{13}H_{16}N_3F]^+$ and $[C_4H_8]^+$, respectively. Both tin–NOR complexes fragment to tin chloride salts and the norfloxacin ligand indicated by the appearance of the same fragmentation lines in the NOR ligand and $[Sn(NOR)_2]Cl_2$, $[Sn(NOR)_3]Cl_4$ complexes. It is reasonable to conclude from the assignment of the fragments that NOR is a bidentate ligand through the oxygen atom of the carbonyl group and one of the oxygen atoms of the carboxylate group in these complexes and the hydrogen atom of the carboxylic group migrates to the piperazinyl group giving the quaternized nitrogen $\{^+NH_2\}$.

The ^1H NMR spectra in DMSO-d_6, figure 8, are in agreement with the suggested coordination through the carboxylate (disappearance of the H (COOH) signal in

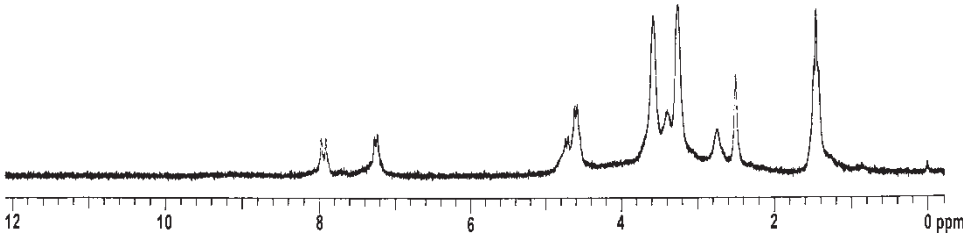

Figure 8. ^{1}H NMR spectrum of $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ complex in DMSO, δ_{TMS}.

Table 3. ^{1}H NMR values (ppm) and tentative assignments for NOR; $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ complex.

NOR	$[Sn(NOR)_2]Cl_2 \cdot 4H_2O$	Assignments
1.13	1.41, 1.43, 1.46	δ H, $-CH_3$
2.0	2.49, 2.74	δ H, $-^+NH_2$
–	3.56	δ H, H_2O
2.78, 3.10, 3.47	4.58, 4.65, 4.70, 4.77	δ H, $-CH_2$ aliphatic
5.93, 7.12, 8.01	7.23, 7.27, 7.90, 7.97	δ H, $-CH_2$ aromatic
11.00	–	δ H, –COOH

our complex) and two peaks at δ 2.49 and 2.74 ppm characteristic for quaternary nitrogen ($-^+NH_2$). The peak characteristic for water molecules was observed at δ 3.56 ppm, not found in the free norfloxacin. The ^{1}H NMR data for free NOR and $[Sn(NOR)_2]Cl_2 \cdot 4H_2O$ are summarized in table 3 and all assignments are given.

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