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Spectroscopic, Thermal Studies and Antimicrobial Activity of Nitrilotriacetates, (NTA)–Ce(III) and –Ce(VI) Complexes

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Two new complexes $[Ce(NTA)(H_2O)_2]$ (**1**), $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (**2**) were obtained during the reactions of metal salts $CeCl_3{\cdot}7H_2O$ and $Ce(SO_4)_2$ with nitrilotriacetic acid, H_3NTA. The infrared and ^1H NMR spectra of the solid complexes have been obtained and assigned. Thermogravimetry, differential thermal gravimetry and differential thermal analyses were also carried out. The data obtained agree quite well with the proposed structures and show that the complexes finally decompose to the corresponding cerium oxides and sulphate. The kinetics of thermal decomposition of the complexes have been studied. The complexes were screened for their antimicrobial activities by the agar-well diffusion technique using DMSO as a solvent against the *E. coli, B. subtilis, P. aereuginosa*, *S. aureus* and fungi: *A. niger, A. fluves; C. albican* and *S. cervisiea*. It has been found that the complexes show a considerable antimicrobial activity.

Key Words: Nitrilotriacetic acid, Ce(III/IV) complexes, Kinetics of thermal decomposition, Antimicrobial activity.

INTRODUCTION

Bioinorganic chemistry has been developing rapidly with special emphasis on metal complexes as therapeutic agents. A broad array of medicinal applications of metal complexes has been investigated and several recent reviews summarize advances in these fields. The interaction of rare earth elements with biological molecules provides a fascinating area of coordination chemistry[1].

Nitrilotriacetic acid (H_3NTA) is a ligand of high biological interest and can form stable species with metal ions in different oxidation state[2-4]. Nitrilotriacetic acid find extensive application in the fields of water and soil treatment[5-9]. It is used primarily as a chelating agent and as a laundry detergent builder. The compound sequesters magnesium and calcium ions present in hard water, thereby reducing buildup and scaling caused by salts of these ions[10]. It is used in detergents after phosphates were banned from detergents, an eluting agent in purification of rare-earth elements, as a boiler feed water additive, in water and textile treatment, in metal plating and cleaning and in pulp and paper processing[10,11]. To a lesser extent, the compound is used in leather tanning, photographic development, synthetic rubber production, the manufacture of pharmaceuticals and in herbicide formulations and micronutrient solutions in agriculture[12,13] as well as in another biological and medical researches[14-19]. Nitrilotriacetic acid also acts as a catalyst for some important chemical processes[20-23]. Nitrilotriacetic acid is one of the most important members, after EDTA in the family of aminopolycarbo-xylic acids. All the members of this family possess in addition to an amino group, at least two carboxylic acid groups. It is a tetradentate ligand with three carboxyl groups and one amino nitrogen atom. Presence of a third acetic acid group renders H_3NTA a good deal more reactive towards the generality of cations than any member of its family[24]. The coordination behaviour of H_3NTA depends on the oxidation state of the metal ion[2,24-28]. The application of spectroscopy to study metal-NTA chelates in aqueous solutions as well as in the solid states provides valuable information about the mode of NTA chelation to metal ions. The anion of NTA is capable of forming 1:2 as well as 1:1 complexes with cations of rare earth metals[29].

Most of the previous work was carried out on nitrilotriacetic acid complexes in aqueous solutions mainly for the determination of stability constants for such complexes[8, 30-35]. The mode of chelation of nitrilotriacetic acid not only depends on the nature of metal cation[25,26] but may be also on the pH at which the syntheses of the complexes is carried out[36]. On the other side, complexes of cerium as an example of rare earth

metals and radioactive rare earth metals were often used for the treatment and diagnose some kinds of tumor[37-39].

The present work deals with the preparation and investigation of nitrilotriacetic acid complexes with Ce(III) and Ce(IV) ions. Our task by this study is to investigate the effect of oxidation state of cerium ion upon the mode of chelation of nitrilotriacetic acid and to investigate the type of bonding and structures of the obtained complexes as well as their thermal behaviour. The infrared and ^{1}H NMR spectra were recorded and assigned along with the thermal properties of cerium complexes as well as the kinetics of thermal decomposition of the complexes. Also, the complexes were screened for their antimicrobial activities.

EXPERIMENTAL

All chemicals used were of high grade. Elemental analyses were carried out in the microanalysis unit of Cairo University, Egypt using CHNS-932 (LECO) and Vario EL elemental analysers. Metal contents and water percentage were determined by thermogravimetric techniques. The results obtained are in good agreement with those calculated for the proposed complexes formulae. Thermal analyses (TG, DTG and DTA) were carried out using a Shimadzu TGA-50 H computerized thermal analysis system. The system includes program which process data from the thermal analyzer with the chromotpac C-R3A. The rate of heating of the samples was kept at 10 ºC/min. Sample masses 2.256 and 2.768 mg for complexes **1** and **2**, respectively were analyzed under N_2 flow at 20 mL/min. α-alumina powder was used as DTA standard material.

The infrared spectra of the reactants and the obtained complexes were recorded from KBr discs using either Perkin-Elmer 1430 or Buck Scientific 500 Infrared spectrophotometers. ^{1}H NMR spectra were recorded on Varian spectrophotometers Gemini 200 and VXR 400 operating at 200 and 400 MHz, respectively using dimethyl sulphoxide-d_6 as a solvent and TMS as an internal reference.

Synthesis of complexes: $[Ce(NTA)(H_2O)_2]$ (**1**). To a hot solution of cerium(III) chloride, $CeCl_3{\cdot}7H_2O$ (372.6 mg, 1 mmol) in dimethyl formaamide-MeOH (1:1, 20 mL), a hot solution of nitrilotriacetic acid, H_3NTA (210.2 mg, 1.10 mmol) in dimethyl formaamide (15 mL) was added. The clear solution was stirred for 4 h at 60 ºC resulting in white powdery precipitate which was filtered off, washed with few drops of Et_2O (3 × 1 mL) and dried under vacuum over P_2O_5. Yield: 180.0 mg (49.41 %). Anal. found (Calcd. for $C_6H_{10}NO_8Ce$, 364.26): C, 19.44 (19.78); H, 2.85 (2.77); N, 3.74 (3.85).

$H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (2): To a hot solution of cerium(IV) sulphate, $Ce(SO_4)_2$ (332.2 mg, 1.00 mmol) in dimethylformaamide-MeOH (1:1, 10 mL), a hot solution of nitrilotriacetic acid, H_3NTA (401.2 mg, 2.10 mmol) in dimethylformaamide (15 mL) was added. The resulting mixture was stirred for 8 h at 70 ºC. The formed faint yellow precipitate was filtered off, washed with few drops of Et_2O (3 × 1 mL) and dried under vacuum over P_2O_5. Yield: 290 mg (54.37 %). Anal. found (Calcd. for $C_6H_{19}NO_{16}SCe$, 533.39): C, 13.48 (13.51); H, 3.70 (3.59); N, 2.70 (2.63); S, 6.13 (6.01).

Antimicrobial activity: The complexes were evaluated for their *in vitro* antibacterial activity against *Bacillus subtilis* NRRL B-94, *Streptococcus aureus* NRRL B-313, *Escherichia coli* NRRL B-3703 and *Pseudomonas aeruginosa* NRRl B-32 and antifungal activity against *Aspergillus niger* NRRL 599, *Aspergillus fluves* NRC, *Saccharomyces cervisiea* NRC and *Candida albicans* NRRL 477 by the agar well diffusion method[40]. Bacteria and the fungi studied were incubated into nutrient broth for 24 h and malt-extract broth for 48 h, respectively. In this method, nutrient agar for bacteria and malt-extract agar sterilized in a flask and cooled to 50 ºC was distributed (50 mL) to sterilized petri dishes (15 cm in diameter) after injecting 0.1 mL cultures of bacterium or fungus, prepared as mentioned above and allowed to solidify. The dilution plate method was used to enumerate microorganisms (105 cells/mL) for 24 h[41]. By using a sterilized proper tubes (6 mm diameter), wells were dug in the culture plates. Complexes dissolved in DMSO were added (200 μ mole/mL) to these wells. The Petri dishes were left at 4 ºC for 2 h and then the plates were incubated at 30 ºC for bacteria (8-24 h) and (72 h) for fungi. At the end of the period, inhibition zones formed on the medium were evaluated as millimeters (mm) diameter. The control samples were DMSO only. The results were compared with a similar run of standard ampicilin, erythromycin (as antibacterial) and fluconazol (as antifungal). Both antimicrobial tests could be calculated as a mean of three replicates.

RESULTS AND DISCUSSION

The reactions at elevated temperature (*ca.* 70 ºC) of Ce(III/IV) [$CeCl_3{\cdot}7H_2O$ and $Ce(SO_4)_2$] with slightly excess amounts of nitrilotriacetic acid in neutral solutions (dmf) resulted in formation of the following complexes, $[Ce(NTA)(H_2O)_2]$ (**1**) and $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (**2**), respectively. Elemental analysis data obtained for complexes **1** and **2** agree quite well with the suggested complexes formulations and confirmed by spectroscopic analysis as well as thermal investigation.

The infrared spectral data for the characteristic bands observed in the complexes spectra are summarized in Table-1 (Fig. 1).

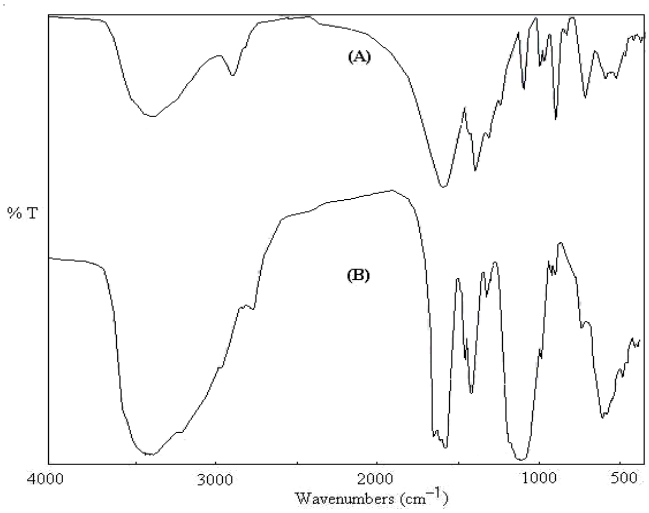


Fig. 1. The Infrared spectra of (A) $[Ce(NTA)(H_2O)_2]$ (**1**), (B) $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (**2**)

The infrared spectrum for the $[Ce(NTA)(H_2O)_2]$ complex shows a strong band in the region of carbonyl stretching

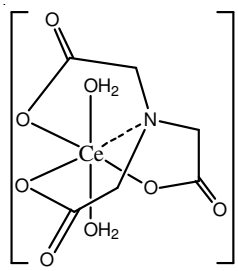
TABLE-1
CHARACTERISTIC INFRARED WAVENUMBERS (cm^{-1}) AND TENTATIVE ASSIGNMENTS FOR THE COMPLEXES $[Ce(NTA)(H_2O)_2]$ (**1**) AND $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (**2**)

Wavenumbers (cm^{-1})			Assignments
H_3NTA	Complex **1**	Complex **2**	
3050, s	3417, br	3412, vs, br	ν(O–H); H_2O
		3239, sh	
		3008, sh	
2998, m	2918, wbr	2927, w, sh	ν(C–H); -CH_2- of NTA
2966, m		2788, vw	
1730, vs	-	-	ν(C=O); free COOH
	1620, vs	1651, vs	ν(C=O); COO–Ce
		1615, sh	
1442, s	1580, sh	1585, vs	C–H deformation;
	1460, sh	1468, ms	-CH_2- of NTA
1337, m	1409, s	1420, s	ν(C–O); COO^-
	1330, m	1332, w	
1243, s	1290, sh		ν(C–C)
	1256, m		
1206, s	1122, m		ν(C–N)
		1180, sh	ν(SO), SO_4^{2-}
		1101, vs, br	
		991, m	
1015, m	1020, m	928, w	C–H bend; -CH_2- and
970, m	990, w	918, w	$\delta_r(H_2O)$
910, m	912, m	818, w	
750, s	732, m	740, m	ν(COC)
	615, m	609, m	ν(Ce–N)
	545, w	562, w	ν(Ce–O)
	478, sh	494, w	
	414, w	457, w	

vibration, ν(C=O). This band is observed at 1620 cm^{-1} and lying in a region typical for coordinated carboxylato group, COO-Ce. The complex spectrum shows also a set of absorption bands at 1409 and 1330 cm^{-1}. These bands could be assigned to the stretching vibration, ν(C-O) of the coordinated carboxylato group. The appearance of these two bands, indicate that in these two complexes there is only one type of the carboxylate group, the coordinated type. The stretching vibration, associated with the C-N bond, ν(C-N) is observed at 1206 cm^{-1} in the spectrum of the free ligand, while the corresponding vibration is observed at 1122 cm^{-1}. This shift *ca.* 84 cm^{-1} to a lower wavenumber can be attributed to the coordination of nitrogen to cerium ions. This conclusion could be supported by observing a medium band at 615 cm^{-1}, which may be attributed to the ν(Ce-N) stretching motions. The Ce-O bonds stretches, ν(Ce-O) are observed as a set of bands lying in the region of 545-414 cm^{-1}.

Nitrilotriacetato in this complex acts as a tetradentate ligand and coordinates to Ce(III) ions through its three oxygen atoms and the nitrogen atom. The same tetradentate coordination mode of NTA was observed with other metal ions[36,42-47] in which NTA occupies four positions of the octahedral coordination sphere and the other two are occupied by two water molecules. The most probable structure according to this behaviour of NTA is shown in **I**.

For Ce(IV) complex, $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (**2**), the infrared spectrum (Table-1), reveals the same pattern with respect to the coordination mode of nitrilotriacetic acid and similar to that reflected by the spectrum of Ce(III) complex. The complex spectrum shows a very strong band with doublet structure at 1651 and 1615 cm^{-1}. This band is attributed to the



(I)

ν(C=O) of the coordinated carboxylato groups, while the ν(C-O) of COO^- groups is observed in the expected region, 1420-1332 cm^{-1}. The cerium(IV)-nitrogen bond stretching vibration is observed at 609 cm^{-1} and cerium(IV)-oxygen bonds stretches as three week bands in the region 562-457 cm^{-1}. Thus, NTA behaves as a tetradentate with the three carboxylato groups, in addition to the nitrogen atom are coordinated to the cerium center and the other two positions are occupied by two water molecules. Very strong and broad absorption band around 1101 cm^{-1} in addition to medium band at 991 cm^{-1} are observed. These bands are due to the stretching vibrations, ν(SO) and characteristic[47] for the ionic sulfate , SO_4^{2-}.

The spectra of both complexes reveal a broad absorption bands at 3417 cm^{-1} due to the stretching vibrations, ν(O-H) of the coordinated water molecules. The assignments of these bands to these wavenumbers are in good agreement with those known for other related complexes[36,42-47].

NMR spectra: ^1H NMR spectra for the obtained complexes are summarized in Table-2. The signals due to methylenic protons, CH_2 of NTA are observed for the free H_3NTA and the complexes in the expected region. The signal due to the O-H protons of carboxylic group, H_3NTA is observed at 12.01 ppm, such signal is disappeared as expected in the Ce(III) complex due to the deprotonation of coordinated carboxylato groups. Very important and informative observation is showed in the spectrum of the Ce(IV) complex, **2**, which is the appearance of a new signal corresponding to one proton at 8.10 ppm. Such signal is not observed in the spectra of either the free ligand or Ce(III) complex and may be assigned to the H^+ [48,49].

TABLE-2
^1H NMR δ VALUES (ppm) of H_3NTA AND ITS CERIUM(III/IV) COMPLEXES **1**, **2** IN DMSO-d_6

Compound	Band assignments*			
	CH_2 (6H)	H_2O	H^+	O–H
H_3NTA	3.49, s	3.55, brs	-	12.01, s
1	3.09, s	3.39, br	-	-
2	3.86, s	3.40, s	8.10, brs	-

*s, singlet; br, broad

Thermal analysis: To make sure about the proposed structures for the complexes under investigation, thermogravimetric analyses TGA, DTG and DTA (Figs. 2 and 3) are measured under nitrogen flow. The thermal data obtained for complexes are summarized and given in Table-3.

The decomposition reactions of $[Ce(NTA)(H_2O)_2]$ (**1**) complex occurs in two steps within the temperature range 90-450 ºC. The first step of decomposition proceeds with a weight loss value of 10 % at a maximum of unexpected low

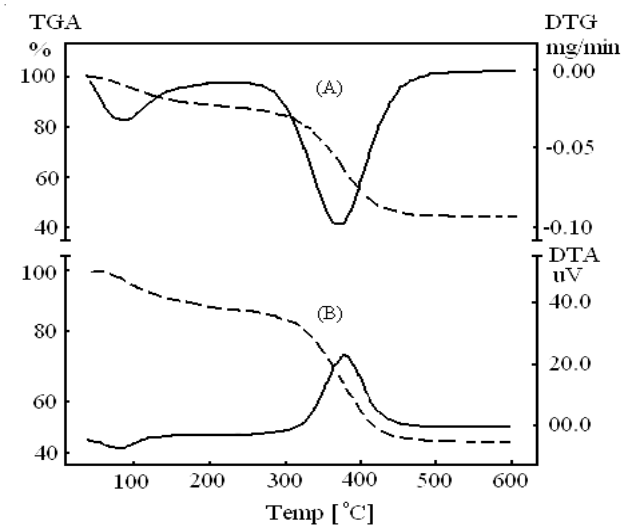


Fig. 2. (A) Thermogravimeteric (TG & DTG) of $[Ce(NTA)(H_2O)_2]$ (**1**); (B) Differential thermal analysis (DTA) for $[Ce(NTA)(H_2O)_2]$ (**1**)

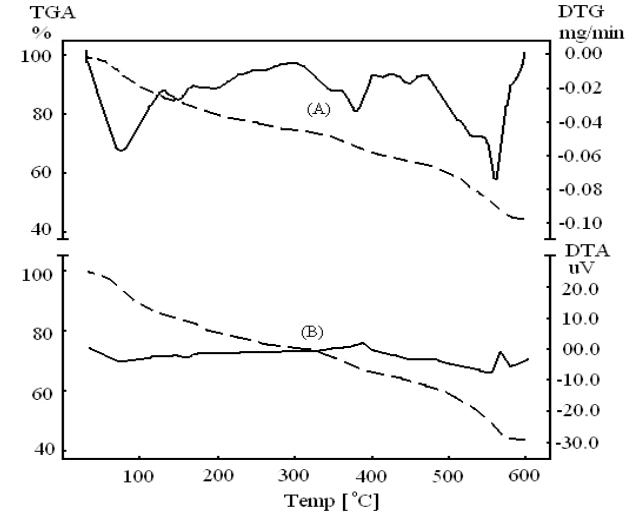


Fig. 3. (A) Thermogravimeteric (TG & DTG) of $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$(**2**); (B) Differential thermal analysis (DTA) of $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$(**2**).

temperature of approximately 90 ºC. This may be associated with loss of the coordinated water molecules, which is in a good agreement with the calculated value of 9.89 %, since this complex contains no lattice water. The second step of decomposition proceeds at a maximum temperature of approximately 375 ºC. This may be attributed to the loss of the organic NTA ligand. The weight loss associated with this step (45.50 %) is in a good agreement with the calculated value of 45.06 %.

The decomposition reactions of $H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (**2**) complex occurred in three steps. The lattice water molecules are lost at a maximum temperature lying at 70 ºC. The obtained weight loss of four water molecules in this complex is 14.00 % (calculated 13.51 %). The second step of decomposition proceeded at a maximum temperature of approximately 147 ºC and associated with a weight loss value of 7 %. This could be attributed to the loss of two coordinated water molecules in good agreement with the calculated value (6.75 %). The final degradation step was observed as three consequent decomposition peaks with maximum temperatures lying in the range of 380-562 ºC. The total weight loss value was 33.00 % associated with the loss of $C_6H_7NO_5$ from HNTA ligand which agrees with the theoretical values of 32.46 %.

Kinetics of the decomposition of the complexes

Determination of reaction order of decomposition: Horowitz and Metzger[50] equation $C_s = (n)^{1/1-n}$, where, C_s is the weight fraction of the substance present at the DTG peak temperature; Ts, is given by

$$C_s = (W_s\text{-}W_f)/(W_o\text{-}W_f) \quad (1)$$

and was used for the determination of the values of the reaction order. Here W_s stands for the weight remaining at a given temperature Ts, *i.e.* the DTG peak temperature, W_o and W_f are the initial and final weights of the substance, respectively. The values of C_s for the thermal decomposition of the complexes for the decomposition steps indicate that the decomposition follows first order kinetics[50,51].

Integral method using the coats-redfern equation: For a first order process the coats-redfern equation[52] may be written in the form:

$$\log\left[\frac{\log(W_f/W_f - W)}{T^2}\right] = \log\left[\frac{AR}{\theta E^*}\left(1-\frac{2RT}{E^*}\right)\right] - \frac{E}{2.303\,RT} \quad (2)$$

where, W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T; ($W_r = W_f\text{-}W$), R is the gas constant, E^* is the activation energy in J mol^{-1}, θ is the heating rate. Since $1\text{-}2RT/E^* \cong 1$, a plot of the left hand side of equation (2) against 1/T was drawn, which gave straight lines where E^* and A (Arrhenius constant) were calculated from the slope and the intercept, respectively.

TABLE-3
THERMAL DATA OF THE DECOMPOSITION OF COMPLEXES **1** AND **2**

Complex	Decomposition temperature (ºC)	T_{max} (ºC)	Species lost	% Weight loss	
				Found	Calculated
$[Ce(NTA)(H_2O)_2]$ (**1**)	90-150	90	$2H_2O$ (coordinated)	10.00	9.89
	300-450	375	$C_6H_6NO_{4.5}$	45.50	45.06
	Total loss			55.50	54.95
	Residue		½ Ce_2O_3	44.50	45.05
$H[Ce(NTA)(H_2O)_2]SO_4{\cdot}4H_2O$ (**2**)	63-128	70	$4H_2O$ (hydrated)	14.00	13.51
	144-202	147	$2H_2O$ (coordinated)	7.00	6.75
	217-567	449	$C_6H_7NO_5$	33.00	32.46
	Total loss			54.00	52.72
	Residue		$CeO(SO_4)$	46.00	47.28

TABLE-4
THERMODYNAMIC PARAMETERS# OF THE DECOMPOSITION OF COMPLEXES **1** AND **2** (THE AVERAGE VALUES ARE GIVEN)

Complex	Decomposition Temp (ºC)	ΔE* KJ mol^{-1}	ϕR^2	ΔS* J K^{-1} mol^{-1}	ΔH* KJmol^{-1}	ΔG* KJmol^{-1}
$[Ce(NTA)(H_2O)_2]$ (**1**)	90-150	28.99	0.99	-181.73	25.98	91.85
	300-450	60.06	0.98	-175.50	54.71	167.73
		Total = 89.05			**80.69**	**259.58**
$H[Ce(NTA)(H_2O)_2]SO_4 \cdot 4H_2O$ (**2**)	63-128	68.02	0.91	-63.67	65.17	87.01
	144-202	44.37	0.97	-165.57	40.87	110.41
	217-567	33.97	0.93	233.70	27.96	196.700
		Total =146.36			**134.00**	**394.12**

#Average value of CR and HM; ϕR^2 = Correlation coefficient

TABLE-5
ANTIMICROBIAL ACTIVITY OF H_3NTA AND ITS CERIUM(III/IV) COMPLEXES

	Diameter of inhibition zone (mm)							
	Bacteria				Fungus		Yeast	
	E. coli	*P. aereuguinosa*	*S. aureus*	*B. subtilis*	*A. niger*	*A. flvus*	*S. cervisiea*	*C. ablicans.*
H_3NTA	06.66±0.140	08.67±0.047	07.33±0.047	05.35±0.099	07.52±0.049	05.720±0.140	00.00±0.000	00.00±0.000
1	13.67±0.048	14.33±0.095	11.67±0.093	11.33±0.047	12.00±0.048	08.35±0.094	10.00±0.043	12.33±0.045
2	12.67±0.094	12.33±0.120	08.39±0.095	10.00±0.094	12.33±0.096	07.35±0.045	09.33±0.023	09.33±0.045
R1	26.66±0.198	28.67±0.092	25.66±0.079	23.66±0.029	00.00±0.000	00.00±0.000	00.00±0.000	00.00±0.000
R2	27.33±0.118	28.66±0.069	27.00±0.045	25.33±0.018	00.00±0.000	00.00±0.000	00.00±0.000	00.00±0.000
R3	00.00±0.000	00.00±0.000	00.00±0.000	00.00±0.000	25.66±0.093	26.33±0.093	28.00±0.046	29.66±0.080

Each value represents mean of sample ± S.D., R1, R2 and R3 represent Ampicilin, Erythromycin and Fluconazol, respectively

Approximation method using Horowitz-Metzger equation: For the first order kinetic process, the Horowitz-Metzger equation[50] may be written in the form:

$$\log\left[\log\frac{W_f}{W_r}\right] = \frac{\theta E^*}{2.303RT_{max}^2} - \log 2.303 \quad (3)$$

where, Ts = DTG peak temperature and $\theta = T - T_s$. A plot of $\log[\log W_f/W_r]$ *vs*. θ will give a straight line and E^* can be calculated from the slope.

The activation entropy ΔS^*, the activation enthalpy ΔH^* and the free energy of activation G^* were calculated using the following equations:

$$\Delta S^* = 2.303\left(\log\frac{Ah}{kT}\right)R \quad (4)$$

$$\Delta H^* = E^* - RT \quad (5)$$

$$\Delta G^* = \Delta H^* - T_s \Delta S^* \quad (6)$$

where, k and h are the Boltzman and Planck constants, respectively.

The thermodynamic parameters are calculated and listed in Table-4. The sums of the activation energies were 89.05 and 146.36 kJ mol^{-1} for the complexes **1** and **2** respectively, which are relatively low. This may be attributed to the ease of decomposition due to sterric hindrance arose from the orientation of the ligand around the metal ion to satisfy the tetradentate coordination along with two coordinated water molecules. This is reflected also from the low values of the sum of enthalpy (ΔH) and the high values of the Gibbs free energy change (ΔG). This also may account for the removal of the water of coordination at relatively low temperature.

Finally, infrared spectra of the final thermal decomposition products for complexes **1** and **2** show the absence of any bands due to lattice water, coordinated water and NTA, but instead the characteristic spectra of cerium oxide and sulfate for complexes **1** and **2**, respectively are observed (Fig. 4).

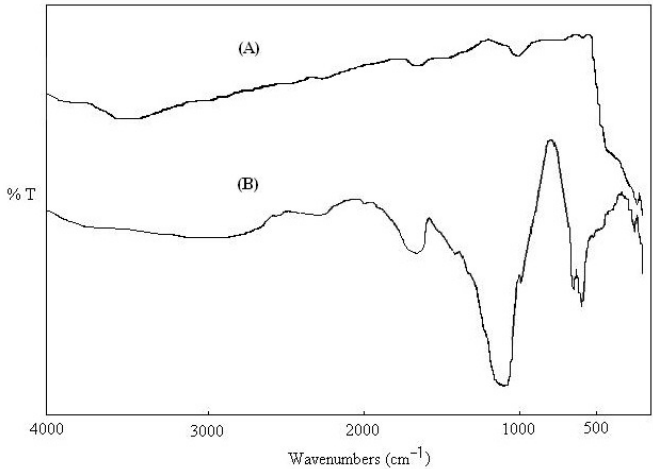


Fig. 4. Infrared spectra of (A) Ce_2O_3 and (B) $CeO(SO_4)$ as a final thermal products for complexes 1 and 2, respectively

Antimicrobial activity: Antimicrobial activities of the ligand and the two complexes have been carried out against the microbial species using nutrient agar medium by the well diffusion method[40]. The comparison of inhibition zone values for the Ce(III/IV) complexes, Table-5 reveals that the antimicrobial activity associated with these complexes could be mainly due to the structure of the complexes and not the oxidation state of the cerium ions. The better activities of the cerium complexes could also be understood in terms of chelation theory[53], which explains that a decrease in polarizability of the metal could enhance the lipophilicity of the complexes. Finally, to complete the evaluation of antimicrobial activity of tested complexes, a comparison with the known antibiotics

was performed and the data are summarized in Table-5. These data show that the effect of complexes against the tested microorganism is lower than the effect of tested antibiotics.

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