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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME NITRILOTRIACETIC ACID–V(III), –Sn(II), –Sm(II) AND –Sm(III) COMPLEXES

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ABSTRACT. Four new complexes $[V(NTA)(H_2O)_2]\cdot H_2O$ (**1**), $H[Sn(NTA)]$ (**2**), $H[Sm(NTA)]\cdot H_2O$ (**3**), and $[Sm(NTA)(H_2O)_2]\cdot H_2O$ (**4**) were obtained during the reactions of metal salts (VCl_3, $SnCl_2\cdot 2H_2O$, $SnCl_4$, $Sm(NO_3)_2\cdot 6H_2O$ and $SmCl_3\cdot 6H_2O$) with nitrilotriacetic acid, H_3NTA. The infrared and ^{1}H-NMR spectra of the solid complexes have been obtained and assigned. Thermogravimetric analyses were also carried out. The data obtained agree with the proposed structures and show that the complexes decomposed to the corresponding metal oxide. The ligand and their metal complexes were screened for their antimicrobial activities by the agar-well diffusion technique using DMSO as a solvent against the following bacterial species: *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa* and antifungal activity against *Aspergillus niger*, *Aspergillus flavus*, *Saccharomyces cerevisiae* and *Candida albicans*. The obtained results were compared with some types of known antibiotics. The minimum inhibitory concentration (MIC) values were calculated at 30 °C for 24–48 h. The activity data show that the complexes are more potent antimicrobials than the parent ligand.

KEY WORDS: Nitrilotriacetic acid, Metal complexes, IR, ^{1}H-NMR Spectroscopy, Thermal analysis, Antimicrobial activity

INTRODUCTION

The ability of the carboxylic acid group to coordinate to metal ions is well known. This property for the carboxylic acid group is reinforced by the presence of a chelation effect and much stronger complexes could be formed by most metal cations. Nitrilotriacetic acid, H_3NTA (**I**) is very important chelating ligand among the family of aminopolycarboxylic acids. H_3NTA complexes have found many applications in the field of water, soil, biological and medical treatments [1].

Investigation on the syntheses and stereochemistry of rare earth metal complexes with aminopolycarboxylic acids has been of much interest to chemists, because many rare earth and radioactive rare earth metal complexes are often used for the diagnosis and treatment of all kinds of cancer [2–4]. Although, lanthanide ions and their complexes have the ability to increase their coordination numbers to more than six [5–10], but the coordination number six (octahedral geometry) is still the most stable one not only for lanthanides but also for the majority of metal cations.

H_3NTA is able to act as tri- or tetradentate ligand depending on the nature of metal cations as well as the experimental conditions [1–14]. In this circumstance, infrared spectroscopy has been shown to be a powerful tool for elucidating the structures of metal complexes with nitrilotriacetic acid. This is achieved by observing the presence or disappearance, upon complexation, of infrared bands corresponding to three states of the carboxylic acid group i) the free uncoordinating, COOH is observed in the range above 1700 cm^{-1}, ii) ionized and coordinating, COO—M in the range 1660–1610 cm^{-1}, and iii) unionized and coordinating group

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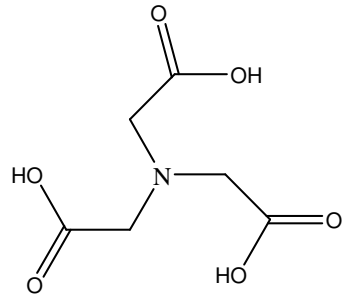
is observed around 1600 cm^{-1} [11]. The mode of chelation of nitrilotriacetic acid not only depends on the nature of metal cation [12, 13] but may be also on the pH at which the syntheses of the complexes are carried out [12, 14].



2,2',2"-Nitrilotriacetic acid (H_3NTA, **I**)

The present article dealt with the preparation and investigation of nitrilotriacetic acid complexes with V(III), Sn(II), Sn(IV), Sm(II) and Sm(III) ions. Our task by this study is to investigate the effect of oxidation state of the metal ion upon the mode of chelation of nitrilotriacetic acid. Their infrared and ^{1}H-NMR spectra were recorded and assigned along with the complexes thermal properties as well as screening for their antimicrobial activities.

EXPERIMENTAL

Materials and spectral measurements

All chemicals used were of high grade. Elemental analyses were carried out in the microanalysis unit of Cairo University, Egypt using CHNS-932 (LECO, USA) and Vario EL elemental analysers (Germany). Metal contents and water percentage were determined by thermogravimetric techniques. The results obtained are in good agreement with those calculated for the proposed complex formulas. Thermal analyses (TG, DTG) were carried out using a Shimadzu TGA-50H computerized thermal analysis system (Japan). The system includes program which process data from the thermal analyzer with the Chromatopac CR-3A (Japan). The rate of heating of the samples was kept at 10 ^oC/ min. Sample masses varied between 1.50 and 3.00 mg were analyzed under N_2 flow at 30 mL/min. The infrared spectra of the reactants and the obtained complexes were recorded from KBr discs using Perkin-Elmer 1430 Infrared Spectrophotometer (USA). ^{1}H-NMR spectra were recorded on Varian spectrophotometer Gemini 200 (Oxford, UK) operating at 200 MHz using dimethylsulfoxide-d_6 as a solvent and TMS as an internal reference.

Synthesis of complexes

*[V(NTA)(H_2O)$_2$]·H_2O (**1**).* To a hot solution of vanadium(III) chloride, VCl_3 (314.6 mg, 2.00 mmol) in dimethylformaamide, DMF (20 mL), a hot solution of nitrilotriacetic acid, H_3NTA (401.4 mg, 2.10 mmol) in DMF (40 mL) was added. The green reaction mixture was stirred for 8 hours at 70 ^oC then, the solution was concentrated to about 5 mL. Addition of excess of Et_2O with stirring resulted in a dark green precipitate that was filtered off, washed with few drops of Et_2O (3 × 1 mL) and dried in vacuo for about 12 hours at *ca* 50 ^oC and then under vacuum over P_4O_{10}. Yield: 300.0 mg (51.18%). Anal. found (calcd. for $C_6H_{12}NO_9V$, 293.10): C**,** 24.56 (24.59); H, 4.50 (4.13); N, 4.86 (4.78).

*H[Sn(NTA)] (**2**)*. To a hot solution of tin(II) chloride, $SnCl_2 \cdot 2H_2O$ (451.3 mg, 2.00 mmol) in DMF (10 mL), a hot solution of nitrilotriacetic acid (401.4 mg, 2.10 mmol) in DMF (20 mL) was added. The reaction mixture was stirred for 20 hours at 80 °C. The formed white gelatinous precipitate was filtered off, washed with few drops of Et_2O (3 × 1 mL) and dried under vacuum over P_4O_{10}. Yield: 410.0 mg (66.59%). It should be mentioned here that, a similar reaction was carried out using $SnCl_4$ instead of $SnCl_2$ and we have obtained the same product (the same elemental analysis, IR and NMR spectra). This implies that Sn(IV) may be reduced to Sn(II) during course of the reaction. Anal. found (calcd. for *H[Sn(NTA)]* (Calcd. for $C_6H_7NO_6Sn$, 307.83): C**,** 22.95 (23.41); H, 2.60 (2.29); N, 4.75 (4.55).

*H[Sm(NTA)]·H₂O (**3**)*. To a hot solution of samarium(II) nitrate, $Sm(NO_3)_2 \cdot 6H_2O$ (382.3 mg, 1.00 mmol) in DMF (10 mL), a hot solution of nitrilotriacetic acid (210.2 mg, 1.10 mmol) in DMF (15 mL) was added. The clear solution was stirred for 18 hours at 70 °C then, the solution was concentrated to 5 mL and left overnight. The formed precipitate was filtered off, washed with few drops of Et_2O (3 × 1 mL) and dried under vacuum over P_4O_{10}. Yield: 120.0 mg (33.57%). Anal. found (calcd. for $C_6H_9NO_7Sm$, 357.50): C, 20.30 (20.16); H, 2.69 (2.54); N, 4.15 (3.92).

*[Sm(NTA)(H₂O)₂]·H₂O (**4**)*. To a hot solution of samarium(III) chloride, $SmCl_3 \cdot 6H_2O$ (364.5 mg, 1.00 mmol) in DMF (10 mL), a hot solution of nitrilotriacetic acid (210.2 mg, 1.10 mmol) in DMF (15 mL) was added. The clear solution was stirred for 14 hours at 70 °C then, the solution was concentrated to 5 mL and left overnight. The formed precipitate was filtered off, washed with few drops of Et_2O (3 × 1 mL) and dried under vacuum over P_4O_{10}. Yield: 190.0 mg (48.41%). Anal. found (calcd. for $C_6H_{12}NO_9Sm$, 392.52): C**,** 18.45 (18.36); H, 3.21 (3.08); N, 3.60 (3.57).

Antimicrobial activity

The ligand and their metal complexes were evaluated for their *invitro* antibacterial activity against *Bacillus subtilis* NRRL B-94, *Staphylococcus aureus* NRRL B-313, *Escherichia coli* NRRL B-3703 and *Pseudomonas aeruginosa* NRRl B-32 and antifungal activity against *Aspergillus niger* NRRL 599, *Aspergillus flavus*, NRC, *Saccharomyces cerevisiae* NRC and *Candida albicans* NRRL 477 by the agar-well diffusion method [15]. 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 °C 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 (10^5 Cells/mL) for 24 h [16]. By using a sterilized proper tubes (6 mm diameter), wells were dug in the culture plates. Complexes dissolved in DMSO were added (200 µmol/mL) to these wells. The Petri dishes were left at 4 °C for 2 h and then the plates were incubated at 30 °C for bacteria (18–24 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, amikacin, erythromycin (as antibacterial) and fluconazol (as antifungal). Both antimicrobial tests could be calculated as a mean of three replicates.

Determination of minimal inhibitory concentration (MIC)

Nutrient and malt-extract agar were employed as basal medium for growth of bacteria and fungi, respectively, during test of complexes **1** and **2**. The culture medium (20 mL) was poured into

Petri dishes (9 mm in diameter) and maintained at 45 ºC until the samples were incorporated into the agar. The samples were added as 1 mL of formulation using an automatic micropipette while constantly stirring to assure a uniform distribution. Each sample was tested at a concentration of 25, 50, 75, 100, 125, 150, 175 and 200 µmol/mL. The different bacterial strains were layered to place 30 µL over the surface of the solidified culture medium containing a sample. After the bacterial were absorbed into the agar, the plates were incubated at 30 ºC for 24–48 h. Bacterial growth was monitored visually and the MIC was determined [17].

RESULTS AND DISCUSSION

Synthesis

The reactions at high temperature (>70 °C) of metal salts (VCl_3, $SnCl_2{\cdot}2H_2O$, $Sm(NO_3)_2{\cdot}6H_2O$ and $SmCl_3{\cdot}6H_2O$) with slightly excess amounts of nitrilotriacetic acid in DMF resulted in the formation of the complexes, $[V(NTA)(H_2O)_2]{\cdot}H_2O$ (**1**), H[Sn(NTA)] (**2**), $H[Sm(NTA)]{\cdot}H_2O$ (**3**), and $[Sm(NTA)(H_2O)_2]{\cdot}H_2O$ (**4**), respectively. Elemental analyses data obtained for the complexes agree quite well with the suggested complexes formulations and confirmed by spectroscopic analysis as well as thermal investigation.

Vibrational spectra

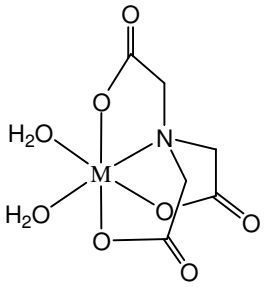
The vibrational spectra obtained for these complexes can be in general, assigned by analyzing the infrared spectra obtained for the carboxylate group in both nitrilotriacetic acid (H_3NTA, the free acid) and metal–NTA chelates. The infrared spectral data for the characteristic bands observed in the complexes spectra are summarized in Table 1.

For V(III) and Sm(III) complexes, $[V(NTA)(H_2O)_2]{\cdot}H_2O$ **(1)** and $[Sm(NTA)(H_2O)_2]{\cdot}H_2O$ **(4)** complexes, the infrared spectra show a strong band in the region of carbonyl stretching vibration, ν(C=O). This band is observed at 1630 and 1648 cm^{-1} for complexes **1** and **4**, respectively. This band is lying in a region typical for coordinated carboxylato group, COO—M. The spectra of complexes also show a set of absorption bands in the region of 1408–1317 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 1124 and 1120 cm^{-1}, respectively. This shift ~ 84 cm^{-1} to a lower wavenumber can be attributed to the coordination of nitrogen to the metal ion. This conclusion could be supported by observing a medium band at 637 and 620 cm^{-1} for the two complexes, respectively, which may be attributed to the ν(M–N) stretching motions. The M–O bonds stretches, ν(M–O) are observed as a set of bands lying in the region of 568–408 cm^{-1}. The spectra of both complexes reveal broad absorption bands at 3445 cm^{-1} for complex **1** and around 3430 cm^{-1} for complex **4** due to the stretching vibrations, ν(O–H) of the coordinated and lattice water molecules. The assignments of these bands to these wavenumbers are in good agreement with those known for other related complexes [14, 18–22]. Nitrilotriacetic acid in these complexes acts as a tetra-dentate ligand and coordinates to V(III) and Sm(III) ions through its three oxygen atoms and the nitrogen atom. The same tetra-dentate coordination mode of NTA was observed with other metal ions [11–14, 18–23] 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 **II**.

Table 1. Characteristic infrared wavenumbers (cm^{-1}) and tentative assignments for the complexes $[V(NTA)(H_2O)_2]\cdot H_2O$ (**1**) , H[Sn(NTA)] (**2**), $H[Sm(NTA)]\cdot H_2O$ (**3**), and $[Sm(NTA)(H_2O)_2]\cdot H_2O$ (**4**).

Wavenumbers[a] (cm^{-1})					Assignements[b]
H_3NTA	**1**	**2**	**3**	**4**	
3050, s	3445, br	3465, br, KBr	3428, br	3559, m 3430, br 3256, mbr	ν(O–H); H_2O
2998, m 2966, m	2968, w 2930, w	2960, m 2929, m	2950,wbr 2927, m	2962, m 2914, m	ν(C–H); -CH_2- of NTA
1730, vs	-	-	-	-	ν(C=O); free COOH
	1630, s	1660, sh 1620, vs	1657, sh 1615, vs	1648, vs 1610, vs	ν(C=O); COO–M
1442, s	1564, vs 1465, m	1470, m 1457, m	1431,ms	1560, m 1469 vs	C–H deformation; -CH_2- of NTA
1337, m	1408, m 1317, m	1400, s 1340, m	1394, ms 1356, m	1407, vs 1353, m 1318, w	ν(C–O); COO^-
1243, s	1270,w 1250, wm	1271, w 1250, w	1297, m 1250, w	1252, m	ν(C–C)
1206, s	1124, w	1115, m	1120, m	1120, m	ν(C–N)
1015, m 970, m 910, m	978, m 910, m	1021, m 914, m 886, m	1022, m 917, m 821, w	1022, m 930, m 912, m	C–H bend; -CH_2- and $\delta_r(H_2O)$
750, s	746, m	757,, m	753, m	760, m	δ(COC)
	637, m	650,m	654,m	620, m	ν(M–N)
	558, w 470, w 408, m	550, m 470, w 430, m	554, w 501, w 425, w	568, w 473, w 428, m	ν(M–O)

a: m, medium; s, strong; vs, very strong; w, weak; br, broad. b: ν, stretching; s, symmetric; as, asymmetric; δ_r, rocking.

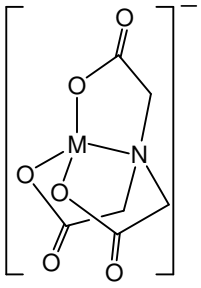


(M = V(III) or Sm(III)

(II)

For Sn(II) and Sm(II) complexes, H[Sn(NTA)] (**2**) and $H[Sm(NTA)]\cdot H_2O$ (**3**), the infrared spectra (Table 1) reveal the same pattern with respect to the coordination mode of nitrilotriacetic acid and similar to that reflected by the spectra of V(III) and Sm(III) complexes. The spectra of complexes show a very strong band with doublet structure at 1660 and 1657 cm^{-1} for the Sn(II) and Sm(II) complexes, respectively. This band is attributed to the ν(C=O) of the coordinated

carboxylato groups, while the ν(C–O) of COO^- groups is observed in the expected region 1400–1340 cm^{-1}. The ν(C–N) is observed as a medium band at 1115 and 1120 cm^{-1}, shifted as expected due to coordination to a lower wavenumbers compared with the free H_3NTA. The metal–nitrogen bond stretching vibration is observed at 650 and 654 cm^{-1} for the two complexes, respectively. The metal–oxygen bonds stretches as three bands for each of week to medium intensities in the region 554–425 cm^{-1}. Thus, according to the foregoing discussion, NTA behaves as a tetra-dentate with the three carboxylato groups, in addition to the nitrogen atom. Considering the steric resistance of NTA to form square planar complexes, the most probable geometry associated with these two complexes is tetrahedral, as shown in structure **III**.



(M = Sn(II) or Sm(II)

(III)

NMR spectra

^{1}H-NMR spectra for the obtained complexes are summarized in Table 2. The signals due to methylenic protons, C*H*$_2$ 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 metal complexes due to the deprotonation of coordinated carboxylato groups. Very important and informative observation is showed in the spectra of the complexes H[Sn(NTA)] (**2**) and H[Sm(NTA)]·H_2O (**3**), this is the appearance of a new signal at 8.23 and 7.95 ppm, respectively. Such a signal is not observed in the spectra of either the free ligand or the other two complexes and may be assigned to the H^+ [24].

Table 2. ^{1}H-NMR δ values (ppm) of H_3NTA and its metal complexes in DMSO-d_6.

Compound	Band assignments			
	C*H*$_2$ (6H)	*H*$_2$O	*H*$^+$	O–*H*
H_3NTA	3.49, s	3.55, brs	-	12.01, s
1	3.03, s	3.37, br	-	-
2	3.88, s 3.95, s	3.43, s	8.23, brs	-
3	3.73, s	3.34, brs	7.95, s	-
4	2.89, s 3.01, s	3.38, br	**-**	-

s, singlet; br, broad; brs broad singlet.

Thermal analysis

To make sure about the proposed structures for the complexes under investigation, thermogravimetric analysis TG, DTG (Figure 1) were measured under nitrogen flow. The thermal data obtained for complexes are summarized and given in Table 3. The decomposition reactions of $[V(NTA)(H_2O)_2]\cdot H_2O$ (**1**) and $Sm(NTA)(H_2O)_2]\cdot H_2O$ (**4**) complexes occur in three expecting stages. The first stage of decomposition proceeds with a weight loss value of 6.50% and 4.50% at a maximum temperature of approximately 121 and 68 ^oC for complexes **1** and **4**, respectively. This stage of decomposition might be associated with loss of the lattice water molecule in good agreement with the calculated values of 6.15 and 4.25% for complexes, respectively. The second stage of decomposition proceeds at a maximum temperature of approximately 165 and 160 ^oC and associated with a weight loss value of 12.40% and 9.30% for complexes **1** and **4**, respectively. This could be attributed due to the loss of two coordinated water molecules in good agreement with the calculated values of 12.29 and 9.18%, respectively. The third stage of decomposition is distributed among three or two steps at a maximum temperature extending from 266 to 583 ^oC, should be due to the loss of the organic ligand, NTA. The weight loss associated with this stage of decomposition (50.10 and 40.20%) is in good agreement with the calculated 50.54 and 42.07% for complexes **1** and **4**, respectively.

Table 3. The maximum temperature values for the decomposition along with the species lost in each step of the decomposition reactions of the obtained H_3NTA complexes.

Complex	Decomposition	T_{max} (^oC)	Species lost	% Weight loss	
				Found	Calc.
$[V(NTA)(H_2O)_2]\cdot H_2O$ (**1**)	1st	121	H_2O	6.50	6.15
	2ed	165	$2H_2O$, coord.	12.40	12.29
	3ed	266 298 496	$C_6H_6NO_{3.5}$	50.10	50.54
	Total loss			69.00	68.98
	Residue		$VO_{2.5}$	31.00	31.02
H[Sn(NTA)] (**2**)		231 321 482 583	$C_6H_7NO_4$	50.00	51.04
	Total loss			50.00	51.04
	Residue		SnO_2	50.00	48.96
$H[Sm(NTA)]\cdot H_2O$ (**3**)	1st	54	H_2O	5.50	5.04
	2ed	236 338	$C_6H_7NO_{4.5}$	47.50	46.19
	Total loss			53.00	51.23
	Residue		$SmO_{1.5}$	47.00	48.77
$[Sm(NTA)(H_2O)_2]\cdot H_2O$ (**4**)	1st	68	H_2O	4.50	4.59
	2ed	160	$2H_2O$, coord.	9.30	9.18
	3ed	397	$C_6H_7NO_{4.5}$	40.20	42.07
	Total loss			54.00	55.84
	Residue		$SmO_{1.5}$	46.00	44.42

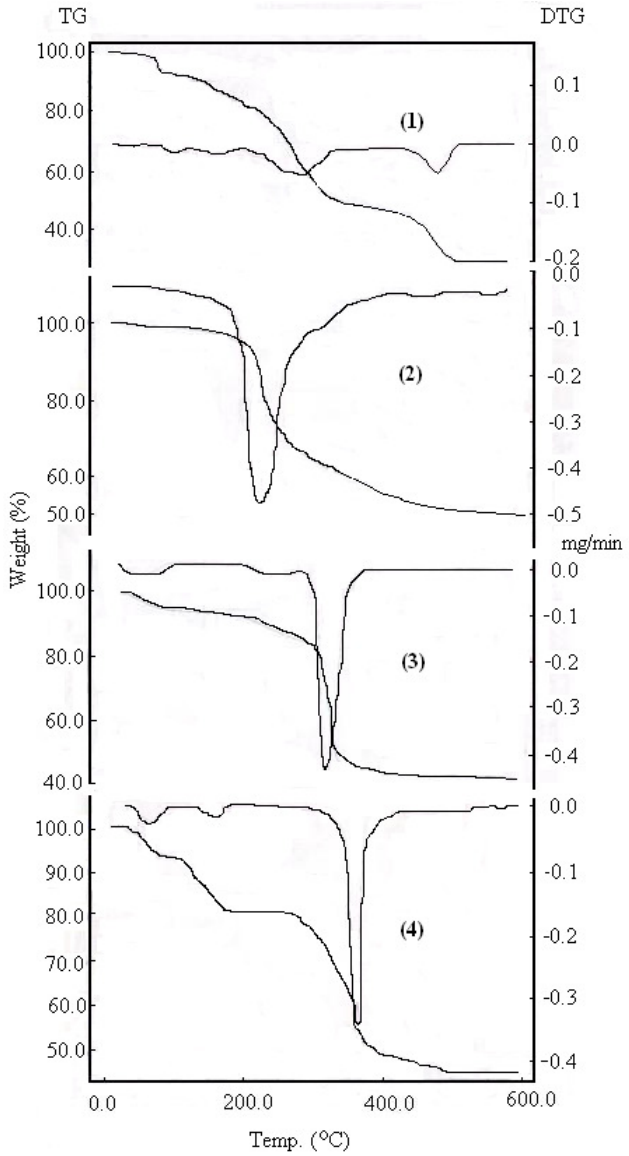


Figure 1. TG and DTG for complexes $[V(NTA)(H_2O)_2]\cdot H_2O$ (**1**), H[Sn(NTA)] (**2**), $H[Sm(NTA)]\cdot H_2O$ (**3**), and $[Sm(NTA)(H_2O)_2]\cdot H_2O$ (**4**).

The obtained data for H[Sn(NTA)] (**2**) and $H[Sm(NTA)]\cdot H_2O$ (**3**) complexes indicate that the decomposition reactions occurred as expected. The lattice water molecule in complex **3** is lost at a maximum temperature lying at 54 °C. The calculated weight loss of one water molecule in this complex corresponds to 5.04% in agreement with the obtained value of 5.50%. Since complex **2** contains no lattice water, it lakes such a step. The main degradation step for both

complexes is observed at a maximum temperature lying in the range of 231–583 °C. The total weight loss values of 50.00 and 47.50% associated with this stage should be due to the loss of $C_6H_7NO_4$ from HNTA of these complexes which agree with the theoretical values of 51.04 and 46.19% for complexes **2** and **3**, respectively.

Finally, infrared spectra of the final thermal decomposition products for complexes **1–4** show the absence of any bands due to lattice water, coordinated water and NTA, but instead the characteristic spectra of metal oxides are observed.

Antimicrobial activity

Concerning the antibacterial and antifungal activity, ligand and their metal complexes were tested against *gram-positive* and *gram-negative* bacteria, yeast and fungi by the well diffusion method [15]. The antimicrobial data were collected in Table 4. The synthesized complexes were found to posses remarkable bactericidal and fungicidal properties compared with the free ligand. The complexes showed inhibition effects on the growth of all the *gram-positive*, *gram-negative bacteria* and fungi, but their efficiency in inhibition was varied from one organism to another. Complex **1** showed higher range of inhibition diameter from 20.00–14.33 mm, whereas complex **2** showed inhibition range of 15.00–8.33 mm. *A. flavus* is more sensitive and *P. aereginosa* is less sensitive to complex **1**. Antibiotic (antibacterial and antifungal) have shown inhibition diameter ranged from 25.66 to 30.66 mm at a concentration of 20 μg/well. A possible explanation for the toxicity of metal complexes can be explained as follows: i) the effect of metal ions on the normal cell process, ii) the polarity of metal ions are considerably reduced on chelation because of partial sharing of its positive charge with a donor groups and iii) possibly π-electron delocalization over the whole molecule. Such molecule increases the lipophilic character of the metal complexes which probably leads to break down of permeability barrier of the cells resulting in interference with normal cell process [25]. Better activities of the metal complexes could also be understood in terms of chelation theory [26], which explains that a decrease in polarizability of the metal could enhance the lipophilicity of the complexes. Complex **1** was found to be more active against the tested microorganisms, whereas, other metal complexes have moderate or less activity. The variation in the effectiveness of different complexes against different microorganisms depends either on the impermeability of the cells of microbes or difference in ribosomes of microbial cells [27, 28].

Table 4. Antimicrobial activity of H_3NTA and its metal complexes.

	Diameter of inhibition zone (mm)							
	Bacteria				Fungus			
	E. coli	*P. aereginosa*	*St. aureus*	*B. subtilis*	*A. niger*	*A. flavus*	*S. cerevisiae*	*C. ablicans*
H_3NTA	4.00±0.05	06.00±0.09	005.00±0.08	00.00±0.05	06.00±0.00	07.00±0.05	00.00±0.00	00.00±0.00
1	14.33±0.12	13.66±0.14	18.66±0.19	18.66±0.17	19.00±0.19	20.00±0.09	18.67±0.12	14.33±0.17
2	08.33±0.05	08.66±0.09	12.33±0.02	09.66±0.12	15.00±0.08	13.00±0.12	14.33±0.09	10.66±0.08
3	07.67±0.14	10.67±0.05	09.33±0.05	08.33±0.09	08.32±0.08	10.17±0.17	00.00±0.00	00.00±0.00
4	14.00±0.09	14.33±0.08	14.33±0.02	09.33±0.05	08.66±0.09	09.66±0.09	00.00±0.00	00.00±0.00
R1	28.66±0.20	29.67±0.09	27.66±0.08	25.66±0.08	00.00±0.00	00.00±0.00	00.00±0.00	00.00±0.00
R2	30.66±0.17	30.33±0.09	28.33±0.09	29.66±0.09	00.00±0.00	00.00±0.00	00.00±0.00	00.00±0.00
R3	29.33±0.12	30.66±0.08	29.00±0.05	27.33±0.02	00.00±0.00	00.00±0.00	00.00±0.00	00.00±0.00
R4	00.00±0.00	00.00±0.00	00.00±0.00	00.00±0.00	26.66±0.09	27.33±0.09	29.00±0.05	30.66±0.08

Each value represents mean of three replicates ±S.D. R1, R2, R3 and R4 represent Ampicilin, Amikacin, Erythromycin and Fluconazol, respectively.

Minimum inhibitory concentration (MIC)

Complexes **1** and **2** were tested at different concentrations for antimicrobial activity. The extent of their inhibitory activities against the tested microorganisms could be understood by comparing the MIC values obtained. Minimum inhibitory concentrations of different microbes are given in Table 5. The results indicated that *E. coli* and *B. subtilis* (MIC: 50 µmol/mL) are more sensitive to complex **1**, and *E. coli* (MIC: 100 µmol/mL) and *A. niger* (MIC: 75 µmol/mL) are more sensitive microorganisms to complex **2**. It is clear from Tables 4 and 5 that inhibitory effect could be attributed to either lipophilicity of the complexes or the cell membrane structure of the microorganism [29].

Table 5. Minimum inhibition concentration (MIC, µmol/mL) of complexes **1** and **2** against some microorganisms.

Complex	Bacteria				Fungus			
	E. coli	*P. aereginosa*	*S.S. aureus*	*B. subtilis*	*A. niger*	*A. flvus*	*C. albicans*	*S. cervisiea*
1	50.00	75.00	75.00	50.00	75.00	50.00	75.00	75.00
2	100.00	150.00	100.00	150.00	75.00	150.00	150.00	150.00

CONCLUSIONS

Four new complexes $[V(NTA)(H_2O)_2]\cdot H_2O$ (**1**), H[Sn(NTA)] (**2**), $H[Sm(NTA)]\cdot H_2O$ (**3**), and $[Sm(NTA)(H_2O)_2]\cdot H_2O$ (**4**) were obtained during the reactions of the corresponding metal salts with nitrilotriacetic acid, H_3NTA and assigned using infrared and ^{1}H-NMR spectroscopy. Thermogravimetric data confirmed the proposed structures and showed that the complexes decomposed to the corresponding metal oxide. The ligand and their metal complexes were screened for their antimicrobial activities by the agar-well diffusion technique. The activity data show that the complexes are more potent antimicrobials than the parent ligand.

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