SYNTHESIS, CHARACTERIZATION, KINETICS, THERMODYNAMICS AND ANTIMICROBIAL STUDIES OF CARBONATOTETRAAMINE COMPLEXES OF Nd(III), Sm(III) AND Gd(III) NITRATES

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Abstract: Carbonatotetraamine complexes of Sm(III), Nd(III) and Gd(III) were synthesized at room temperature. The complexes were characterized by molar conductivity, colour, solubility test and spectrometrically(IR and UV-Vis). The kinetics of complex formation were studied by determining the amount of complex formed with time at different temperatures. The graph of semi-log of yield in mole against time of the various complexes were plotted to obtain the observed rate constants (k_{obs}) which were used to plot $\ln k_{obs}$ versus 1/T to obtained activation energy (E_a). Thermodynamics parameters were obtained from plots of $\ln(k_{obs}/T)$ versus 1/T and antimicrobial activities of the ligand and its complexes were tested using Agar-well diffusion techniques for zone of inhibition while Agar-dilution techniques was used for minimum inhibitory concentration and bactericidal or fungicidal concentration. The solubility results showed complexes were slightly soluble in formaline, phenylhydrazine and dichloromethyl while the complexes had molar conductivity of 2.7 – 5.6 µS which implied their non-electrolytic nature. The UV spectra suggested octahedral geometries for the complexes. The complexes formed where of the general formula ML where L is the ligand and M is the respective Ln^{3+} metal ions and the activation energy (E_a) obtained were 24.743, 8.913 and 29.706 kJ for Nd(III), Sm(III) and Gd(III) Complexes which were positive E_a indicating that, the rate of formation increased with increasing temperature. The kinetic results showed that increase in time and temperature increases the yield of the complexes. The results of thermodynamics parameters showed that; the Gibbs free energy change (ΔG^o) of the complexes were -334.370, -293.250 and -344.600 $kJmol^{-1}$ which proved the formation of the complexes were spontaneous, the enthalpy change (ΔH^o) were -21.915,-1.464 and -27.054 $kJmol^{-1}$ for Nd(III), Sm(III) and Gd(III) respectively showing the enthalpy is the driving force for the formation of the complexes. However the positive result of the entropy change (ΔS^o) which were 1.031, 0.963 and 1.048 $kJmol^{-1}$, respectively suggest that entropy was responsible for the complexation process. All the complexes were found to inhibit the growth of *E. coli*, *S. aureus*, *S. typhi*, *A. niger*, *T. rubrum* and *Candida albicans*in the order of SM>Gd>Nd. The complexes displayed higher inhibition zones on the bacteria strains than the fungi strains. The MIC confirmed that the complexes will be more effective against the studied bacterial infections. The complexes were bactericidal and fungicidal showing that they could serve as raw materials for synthesis of new drugs.

Keywords: Carbonatotetraamine, Nd(III), Sm(III), Gd(III); Antimicrobial studies

Introduction

Discoveries in bioinorganic chemistry have shown that many lanthanide metals have an important place in medicinal chemistry. Complexes obtained from lanthanides and Schiff base ligands have been studied and known to show pharmaceutical and clinical properties such as analgesics, anti-inflammatory, ulcerogenic, antidiabetic, antimicrobial, anticancer activities and for treatment of neurological disorders (Osowole *et al.*, 2012).A large number of the metal complexes are used as catalysts in many organic reactions such as polymerization, hydrolysis, hydrogenation and cross coupling reactions. Schiff base metal complexes derived from sulfanethiadizole and salicyaldehyde have been known to have increased insecto-arachnicidal activities and thus destroy a large number of insects. They are also known to assist plant growth and regulate the activities of auxin and cytokine. Also, metal complexes of the azomethine origin have been used to dye leather, food packages and wool (Kumar *et al.*, 2013). Transition metal complexes have played a significant role in the enormous growth of the field of catalysis. Metal ligand complexes found to catalyze Heck and Suzuki reactions which were tested via Palladium (II) complex of N, N, O, O-Schiff base ligand (Naziah *et al*., 2012).

Better antimicrobial activity is revealed when metal ions react with ligands compared to when the ligands are free (uncoordinated) and this warrants the investigation of recent drugs with undiscovered mechanism of action against pathogenic bacteria. The use of these new compounds is likely to have great potential against pathogenic bacteria; nonetheless, the need for new methodologies of evaluation of antimicrobial activity cannot be relegated to the background (Pourjavid *et al*., 2012; Malik *et al.*, 2018; Iorungwa *et al*., 2019).

Several studies have revealed that by condensation of salicylaldehyde with different heterocyclic compound and their derivative with potent antibacterial and antifungal activity obtained (Xavier *et al.*, 2012). Thiadizolederivative compound of salicylaldehyde was prepared and found to be highly potent antibacterial against *Bacillus cereus* and antifungal against *Aspergillus niger*. Several compound incorporating piperazinyl guanidine. When condensed with Salicylaldehyde were found to exhibit cardiovascular and vasodepressive antimicrobial activity (Xavier *et al.*, 2012).

As a result of the implicit focus created by transition metal complexes of Schiff base and some Schiff base complexes as instruments for analysis of pharmacological constituents with respect to biological activity; the major objective of this paper is to synthesize, characterize and undertake kinectics, thermodynamics and antibacterial studies of carbonatotetraamine complexes of Nd(III), Sm(III) and Gd(III) nitrates.

Materials and Methods

Chemicals, reagents and apparatus

The reagents and solvents used include; distilled water, glacial acetic acid, Nd(III)nitrate, Sm(III)nitrate, Gd(III)nitrate, hydrogen peroxide, methanol, ethanol, acetone, dimethylsulphoxide (DMSO), dimethylformamide (DMF). All the chemicals were of analytical grade obtained from Sigma Aldrich. Gallenkamp melting point apparatus with digital thermometer, conductivity meter, Perkin Elmer FT-IR spectrophotometer, Perkin Elmer spectrophotometer UV-VIS

double beam PC scanning spectrophotometer.

Synthesis of carbonatotetraamine Ligand

Ammonium carbonate (0.960 g, 0.01 mol) was dissolved in 60 mL of water. To this solution, 60 mL of concentrated aqueous ammonia solution was added. Few drops of hydrogen peroxide was added to the mixture and stirred for 3 h. The resulting precipitates were collected by filtration, washed with cold water and ethanol and allowed to dry in a dessiccator containing fused calcium chloride (Jaffray *et al*., 2005). The percentage yield was calculated using the formula:

$$\text{Percentage yield} = \frac{Experimental\ yield}{Theoretical\ yield} \times 100\% \quad \ldots\ldots\ldots 1$$

Synthesis of carbonatotetraamine metal(III) complexes

Synthesis of carbonatotetraamine neodymium(III)nitrate $[Nd(NH_3)_4CO_3]NO_3$

Dissolved (0.960 g, 0.01 mol) of ammonium carbonate in 60 mL of water was added to 60 mL of concentrated aqueous ammonia. A second solution was prepared by dissolving neodymium(III) nitrate hexahydrate (2.07 g, 0.005 mol) in 30 mL of water. With stirring, the first solution was added to the second solution, and then followed by 8 mL of 30% hydrogen peroxide. The resulting solution was placed on a hot plate and stirred for three hours. While solution was still hot, vacuum filtration and cooling of the filtrate in an ice–water bath was carried out. Red crystals were precipitated out, and were collected by vacuum filtration. The crystals were washed with ice cold water and thereafter with ethanol. The mass of crystals collected was recorded (Abuh, 2019). The percentage yield was calculated from equation (1)

The equation for the reaction is:

$$Nd(NO_3)_3.\ 6H_2O + 4NH_3 + (NH_4)_2CO_3 + H_2O_2 \rightarrow [Nd(NH_3)_4CO_3]NO_3 + NH_4NO_3 + 6H_2O \quad \ldots\ldots\ldots 2$$

Synthesis of carbonatotetraamine samarium(III)nitrate $[Sm(NH_3)_4CO_3]NO_3$

Exactly 60 mL of concentrated aqueous ammonia solution was made and added to an already prepared (0.960 g, 0.01 mol) of ammonium carbonate in 60 mL of water. A solution made by adding (2.09 g, 0.005 mol) of Sm(III)nitrate hexahydrate in 30 mL of water was also made and added to the first solution, stirred using a magnetic stirrer for 3 h and the precipitate formed was collected after filtration then kept to dry in a dessicator (Jaffray *et al.*, 2005). The equation for the reaction is:

$$Sm(NO_3)_3.\ 6H_2O + 4NH_3 + (NH_4)_2CO_3 + H_2O_2 \rightarrow [Sm(NH_3)_4CO_3]NO_3 + NH_4NO_3 + 6H_2O \quad \ldots\ldots\ldots 3$$

The percentage yield was also determined using equation (1)

Synthesis of carbonatotetraamine gadolinium(III)nitrate $[Gd(NH_3)_4CO_3]NO_3$

The Gd(III) complex of the ligand was prepared by slowly adding a solution of (2.11 g, 0.005 mol) gadolinium (III) nitrate hexahydrate into the already prepared (0.960 g, 0.01 mol) of ammonium carbonate in 60 mL of water and concentrated aqueous ammonia then followed by 8 mL of 30% hydrogen peroxide. The resulting mixture was stirred with a magnetic stirrer for 3 h and the precipitate formed was collected by filtration, rinsed using water followed by ethanol and was allowed to dry in a dessiccator containing fused calcium chloride. The percentage yield was also from equation (1).

The equation for the reaction is:

$$Gd(NO_3)_3.\ 6H_2O + 4NH_3 + (NH_4)_2CO_3 + H_2O_2 \rightarrow [Gd(NH_3)_4CO_3]NO_3 + NH_4NO_3 + 6H_2O \quad \ldots\ldots 4$$

Solubility tests

About (0.01 g) of the prepared complexes were added to 10 cm^3 portions in separate test tubes containing of each of the solvents (distilled water, methanol, ethanol, dimethylsulfoxide, dimethylformamide and acetone) and shaken vigorously. If the entire solute dissolved to give a homogenous mixture after shaking the sample was considered soluble (S). However if some dissolved and some were left, the sample was considered to be slightly soluble (SS). If the solute remained as introduced then it means it is insoluble (INS) (Iorungwa *et al*., 2019).

Melting point determination

A sample of the metal (III) complexes was put into separate capillary tubes and each inserted into the heating block and heated one after the other and the temperature at which each of the sample melted was recorded from the digital screen.

Molar conductivity measurement

The molar conductivities of the Schiff bases along with the respective complexes were obtained from DMSO using a conductivity meter.

Infrared and electronic spectra data

The infrared spectral data of the synthesized metal complexes was run as KBr discs and displayed on Perkin Elmer FT-IR spectrophotometer spectrum BX with spectrum version 5.3.1 software version. The ultraviolet spectral of the prepared ligand along with the complexes were obtained using acetone as solvent from Perkin Elmer UV-VIS double beam PC scanning spectrophotometer (UV-Winlab 2.8.5.04) software version.

Kinetic and thermodynamic data

Dissolved (0.960 g, 0.01 mol) of ammonium carbonate in 60 mL of water was added to 60 mL of concentrated aqueous ammonia. A second solution was prepared by dissolving an accurate amount of metal salts in 30 mL of water. With constant stirring, the first solution was added to the second solution, and then followed by 8 mL of 30% hydrogen peroxide and the mixture was placed on a SB160 heat-stirrer. The stirrer was set at 1900 rpm and the mixture was heated at temperatures of 35, 45, 55 and 65°C, this was maintained for the required time of 40, 60, 80, 100 and 120 min. The precipitates obtained were filtered off, washed with hot ethanol, ether and dried under vacuum at 70°C and weighed. The various weight obtained were analyzed to ascertain the yield in mole. The graphs of semi- log of yield in mole against time were plotted to obtain observed rate constants which were eventually used to plot $\ln k_{obs}$ vs. 1/T to obtain activation energy (E_a) and $\ln(k_{obs}/T)$ vs. 1/T to obtain thermodynamic parameters (Iorungwa *et al*., 2019).

Antimicrobial studies

The antimicrobial study was conducted in the microbiology laboratory of University of Agriculture, Makurdi using the Agar-well diffusion technique.

Test for zone of inhibition (bacteria)

The bacteria culture media was done as described by Aliyu*et al*., (2011). A stock solution of the antimicrobial agent was prepared by dissolving 1 g of the substance in 10 mL of 20% dimethylsulphuroxide (DMSO) to give a stock solution of 100 mg/mL. 1 mL of the broth inoculums(microbial specie inoculated in normal saline and incubated 24 h) was dispensed into a sterile Muller Hinton Agar (Himedia, India) was poured into the plate and mixed properly (pour-plate method) and allowed to gel. A sterile cork borer, 6 mm in diameter was used to bore wells on the plate and 20 µL of the stock antimicrobial agent was dispensed into the wells and labelled properly. The plates were allowed to stand for 30 min to allow the antimicrobial agent diffuse into the agar. The plates were packed, wrapped and incubated at 37°C for 24 h for bacteria. After incubation, the zone of inhibition was measured in millimetre (Aliyu *et al*., 2011).

Test for Zone of inhibition (fungal)

The method for testing the antifungal activity as described by Aliyu *et al*. (2011) was as followed. A stock solution of the antimicrobial agent was prepared by dissolving 1 g of the substance in 10 mL of 20% dimethylsulphoxide (DMSO) to

give a stock solution of 100 mg/mL. 1 mL of the broth microbial species inoculated in normal saline and incubated 24 hr was dispensed into a sterile Petri dish after which about 20 mL of sterile Mueller Hinton agar was poured into the plate and mixed properly and allowed to gel. A sterile cork borer, 6 mm in diameter was used to bore a well on the plate and 20 µL of the stock antimicrobial agent was dispensed into the wells and labelled properly. The plates were allowed to stand for 30 min to allow the antimicrobial agent diffuse into the agar. The plates were packed, wrapped and incubated at 72 h at room temperature. After incubation, the zones of inhibition were measured in millimetre using transparent rule and recorded (Aliyu *et al*., 2011).

Minimum inhibitory concentration (MIC) and minimum bactericidal or fungicidal concentrations (MBC/MFC)

The MIC was carried out based on the method described by Aliyu *et al*. (2011) using Agar-dilution techniques varying concentrations of the antimicrobial agent was prepared in an agar by mixing different proportions of the Muller Hinton agar and the stock solution of the antimicrobial agent. The following combinations were done 6:6 mL, 3:9 mL, 1.5:10.5 mL and 0.75:11.25 mL of antimicrobial agent and mueller Hinton agar respective thereby giving the following percentage concentrations 50, 25, 12.5 and 6.25%, respectively. The organisms were spot inoculated on all the concentrations and incubated for24 and 72 h for bacteria and fungi incubation, the plates were checked for growth. The minimum concentration at which completely inhibited the activity of the organism was recorded as the minimum bactericidal or fungicidal concentration (MBC/MFC) while the minimum concentration which did not completely inhibit activity of the organism but did not expand beyond the spot of inoculation was recorded as the MIC(Aliyu *et al*., 2011).

Results and Discussion

Physical properties of the Ligand and its complexes

The physical properties of the synthesized ligand along with the complexes such as colour, melting point (°C), molar conductivity (µs) are presented in Table 1.

Table 1: Physical data of the synthesized carbonatotetramine complexes

Compounds	Colour	Conductivity (µs)
Nd(III) complex	Red	2.7
Sm(III) complex	Purple	5.6
Gd(III) complex	White	3.1

The physical properties obtained for the compounds showed that all the synthesized compounds were variedly coloured and existed in powdery form indicating their polymeric nature (Iniama*et al.*, 2018).The molar conductance values were very low in the range of (2.7-5.6 µs). The high melting points displayed by the complexes suggested strong metal-ligand bonds (Didarul *et al.*, 2010). The low conductivities displayed by the compounds were indications that the compounds were non-electrolytic. This means that the degree of dissociation of the compounds was low and therefore fewer ions were in solution (Ogunniran *et al.*, 2008). The complexes were insoluble in water, ethanol, methanol, acetone DMF and DMSO and partially soluble in Formaline, Phenylhydrazine and Dichloromethyl as seen in Table 2. The complexes were all stable as they did not decompose while being stored in a dessiccator for over four weeks (Iniama and Iorkpiligh, 2018).

Table 2: Solubility data of the synthesized complexes at room temperature

Compounds	Distilled water	Ethanol	Methanol	Acetone	DMSO	Formaline	Phenylhydrazine	Dichloromethyl
Nd(III) complex	INS	INS	INS	INS	INS	SS	SS	SS
Sm(III) complex	INS	INS	INS	INS	INS	SS	SS	SS
Gd(III) complex	INS	INS	INS	INS	INS	SS	SS	SS

SS= slightly soluble INS=Insoluble

Table 3: Infrared spectra of the synthesized complexes

Compounds	v(NH_3)	v(C=O)	v(COO^-)	v(M-N)	v(M-O)
Sm(III) complex	3465s	1517s	1445s	715m	387
Nd(III) complex	3346s	1532s	1433s	484m	424
Gd(III) complex	3335s	1505s	1403s	688m	466

s = strong, **m**=medium, **w**= weak

Table 4: Electronic spectra of the synthesized complexes

Compounds	Absorbance (nm)	Wavelength (nm)	Bands (cm^{-1})	Assignment	Geometry
Sm(III) complex	6.00	384	26,041	π- π*	
	1.03	558	17,921	$^6H_{5/2}\rightarrow{}^6P_{3/2}$.	Octahedral
Nd(III) complex	6.00	369	27,100	π- π*	
	2.21	562	17,793	$^4I_{9/2}\rightarrow{}^4G_{5/2}$	Octahedral
Gd(III) complex	2.69	393	25,445	π- π*	
	2.18	452	22,123	$^8S_{7/2}\rightarrow{}^6D_{5/2}$,	Octahedral

Infrared spectra data of the synthesized compounds

The infrared spectra data of the synthesized complexes were recorded within the range of 350-4000 cm^{-1}. The infrared spectra data is a very important tool in structural elucidation as it gives the functional groups present in a compound. Table 3 displayed some selected vibrational bands representing respective functional groups present in the complexes. Formation of bonds on coordination was elucidated by critical observation and comparing with other related literature. Based on these a tentative structure was proposed for the complexes. The infrared spectral of the complexes presented prominent vibrational bands at 3465, 3364 and 3335 cm^{-1} for the Sm, Nd and Gd complexes respectively. These bands were assigned the stretching NH_3 vibrations (Pavia, 2001). The strong vibrational bands seen at 1517, 1532 and 1505 cm^{-1} in the spectra of Sm, Nd and Gd complexes respectively were due to the carbonyl (C=O) vibration (Iniama *et al.*, 2014). This strong carbonyl vibration is in the range of aliphatic carbonyl vibration and lower than the keto C=O vibrations (1700-1800 cm^{-1}). This strong absorption bands presented by the C=O groups of the complexes is due the greater electronegativity of the oxygen atom compared to the carbon atom (Iniama *et al.*,

2018). This higher electronegativity of the oxygen atom made it pull the bonding electrons in the C=O towards itself and away from the carbon atom. This in turn increases the polarity of the C=O band making it to absorb strong (Iniama *et al.*, 2018). This effect will then make the carbon atom to be electron deficient and thus will withdraw bonding electrons from any neighbouring atom or group next to it. (Sharma *et al*., 2013).The carboxylic (COO^-) vibration of the Sm, Nd and Gd complexes were formed at 1445, 1433 and 1403, respectively (Malik *et al*., 2018). The metal-nitrogen (M-N) vibrational bands of the complexes were seen at 715, 484 and 688 cm^{-1} in the spectra of Sm, Nd and Gd, respectively. The bands at 387, 424 and 466 cm^{-1} on the infrared spectra of Sm, Nd and Gd complexes were assigned to the metal oxygen (M-O) bond (Iniama *et al.*, 2018). These M-N and M-O bands did not appear as weak bands showing that a strong bond was formed between the metal ions and the ligand. This was in agreement with the high melting points obtained for the complexes (Avila *et al*., 2017).

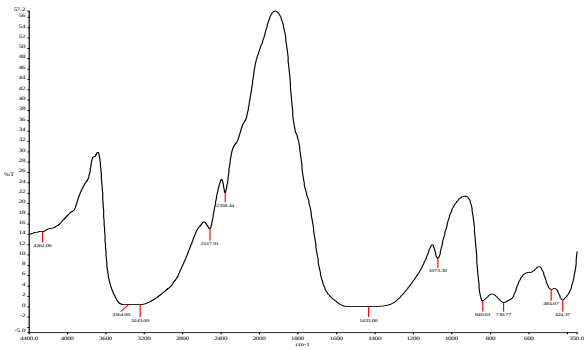

Fig. 1: IR spectra of Nd(III) complex

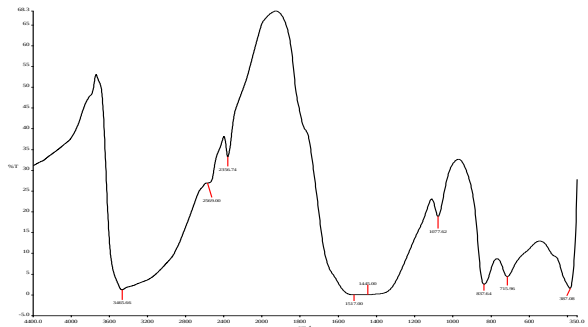

Fig. 2: IR spectra of Sm(III) complex

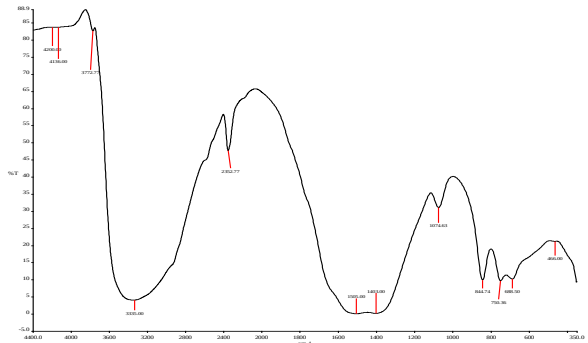

Fig. 3: IR spectra of Gd(III) complex

Electronic spectral data of the synthesized compounds

The electronic absorption spectra are important to the study of metal complexes because they give additional information necessary to evaluate the results obtained. This information is therefore used to elucidate electronic transitions and the stereochemistry to the compounds formed (Raman *et al.*, 2004). The *f-f* orbitals of the Ln^{3+} complexes are deep inside the metals and this makes the crystal field effect to be significantly smaller compared to the *d* block complexes. The lanthanide ions do not contribute appreciably to the spectra of their complexes since the *f-f* transitions are Laporte forbidden (Gueyea *et al*., 2017). For this reason, the *f-f* absorptions are very weak bands compared to the ligand metal charge transfer (Geethalaksmi and Theivarasu, 2016).

The Sm(III) is known with a d^5 configuration, which confers stability. The electronic spectrum of Sm complex had its *d-d* absorption at 17,921 cm^{-1}due to $^6H_{5/2}\rightarrow{}^6P_{3/2}$. This transition is a characteristic of octahedral Sm complex. The observed *f-f* transitions for Nd(III) complex was seen at 17,793 cm^{-1}. This transition was assigned to $^4I_{9/2}\rightarrow{}^4G_{5/2}$, which is compatible with an *f* octahedral geometry of Nd(III) complex. The spectra of Gd complex showed its absorption at 22,123 cm^{-1}. This was down lined to $^8S_{7/2}\rightarrow{}^6D_{5/2}$, which fingers octahedral Nd(III) complex .

Kinetics studies of the complexes

The kinetic studies investigated the effects of temperature on the amount of metal complex formed at various time. The plots of semi-log of the yield of metal complexes in mole against time showed an increase in the observed rate constant of the formation of complexes which indicate an increase in the amount of complexes formed as temperature and time increased. The activation energy (E_a) of various complexes was determined from the slope of the plots of $\ln k_{obs}$ against 1/T.

Figures 4, 5 and 6 show the semi-log plots of Nd(III), Sm(III) and Gd(III)complexes yield in mole with time at different temperatures. The three plots showed an increase in observed rate constants of the formation of the three complexes as temperature increased. This means the rate of formation of these complexes depends on the temperature at which it is run. As the temperature increased, the molecules of reactants move faster and therefore collide more frequently. The molecules also carry more kinetic energy. Thus, the proportion of collisions that overcome the activation energy for the formation increases with temperature. This, therefore, allows for the complexes to be formed faster (Toan *et al.*, 2011).

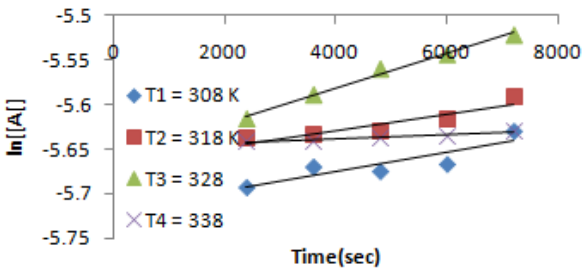

Fig. 4: Semi-log plots of Nd(III) complex yield with time at different temperatures

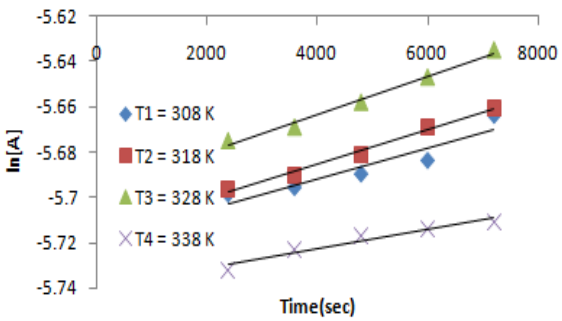

Fig. 5: Semi-log plots of Sm(III) complex yield with time at different temperatures

Figure 7 shows the semi-log plots of the observed rate constant of Nd(III), Sm(III) and Gd(III)complexes against temperature inverse ($\ln k_{obs}$vs. 1/T). The values of activation energy (E_a) obtained from the plots were 24.743, 8.913 and 29.705 kJoules for Nd(III), Sm(II) and Gd(III)complexes respectively which were positive activation energy (E_a) indicating that, the rate of the formation increased with increasing temperature and the "apparent" rate constant of the overall formation-defined by Arrhenius behaviour will increase as temperature is increased and is a signal that the formation of the complexes has no complex mechanism and the relative higher activation energy of Gd(III) explained the small yield of Gd(III)complex at some temperature because only a very small fraction of collision would have enough energy to overcome activation energy (Ohia *et al*., 2013).

Table 1: The rate constant observed at various temperatures for Nd(III) complex

T (K)	K_{obs}x 10^{-5}	K_{obs}/T x 10^{-8}	lnK_{obs}/T	lnK_{obs}	1/T (K^{-1})
308	1.00	3.25	-17.24	-11.51	0.00325
318	1.50	4.72	-16.87	-11.11	0.00315
328	2.00	6.10	-16.61	-10.82	0.00305
338	2.00	5.92	-16.64	-10.82	0.00296

Table 2: The rate constant observed at various temperatures for Sm(III) complex

T (K)	K_{obs}x 10^{-6}	K_{obs}/T x 10^{-8}	lnK_{obs}/T	lnK_{obs}	1/T (K^{-1})
308	7.00	2.27	-17.42	-11.87	0.00325
318	8.0	2.52	-17.50	-11.74	0.00315
328	9.00	2.74	-17.41	-11.62	0.00305
338	9.50	2.81	-17.39	-11.56	0.00296

Table 3: The rate constant observed at various temperatures for Gd(III) complex

T (K)	K_{obs} x 10^{-5}	K_{obs}/T x 10^{-8}	lnK_{obs}/T	lnK_{obs}	1/T (K^{-1})
308	1.00	3.25	-17.24	-11.51	0.00325
318	1.50	4.72	-16.87	-11.11	0.00315
328	1.80	5.49	-16.72	-10.93	0.00305
338	3.00	8.88	-16.23	-10.41	0.00296

Table 4: Thermodynamic parameters for formation of Nd(III), Sm(III) and Gd(III) complexes

Complex	ΔH° (kJmol^1)	ΔG° (kJmol^1)	ΔS° (kJmol^1)	Ea (kJ)
Nd(III)Complex	-21.916	-334.370	1.031	24.743
Sm(III)Complex	-1.464	-293.250	0.963	08.913
Gd(III)Complex	-27.054	-344.600	1.048	29.705

Thermodynamics studies of the complexes

Thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°) change of activation during the formation of the complexes can be evaluated from the following equation:

$$\ln\left(\frac{Kobs}{T}\right)=\ln\left(\frac{Kb}{h}\right)+\frac{\Delta S^o}{R}-\frac{\Delta H}{RT} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$\Delta G^o = \Delta H^o - T_a\Delta S^o \quad \text{(Iorungwa}et\ al.\text{, 2014)} \ldots\ldots\ldots (2)$$

Where k_{obs} = observed reaction rate constant, T = Temperature (K), T_a= the absolute temperature at which reaction can occur, k_b = Boltzmann constant, h = Planck's constant, R = Gas constant ($Jmol^{-1}K^{-1}$), ΔG° = The Gibbs free energy of activation ($kJmol^{-1}$), ΔH° = the enthalpy of activation ($kJmol^{-1}$) and ΔS°= the entropy of activation ($kJmol^{-1}$).

The values of ΔH° and ΔS° were determined from the slope and intercept of the plots of $\ln\left(\frac{Kobs}{T}\right)$ vs$\frac{1}{T}$ (Fig. 7). The values of ΔG° were calculated from equation (2). The values of the enthalpy change of activation (ΔH°), the entropy change of activation (ΔS°) and the Gibbs free energy of activation (ΔG°) found in this work were -21.915, 1.031 and -334.37 $kJmol^{-1}$ for Nd(III) while -1.464, 0.963 and -293.25 $kJmol^{-1}$for Sm(III) and -27.054, 1.048 and -344.600 $kJmol^{-1}$ for Gd(III) complexes.

The negative values of ΔG° showed the formation of the complexes was spontaneous in nature. The negative value of enthalpy change of formation (ΔH°) of the complexes implies that the enthalpy is the driving force for the formation of the complexes. However, the positive values of entropy (ΔS°) shows that entropy is responsible for the complexation process.

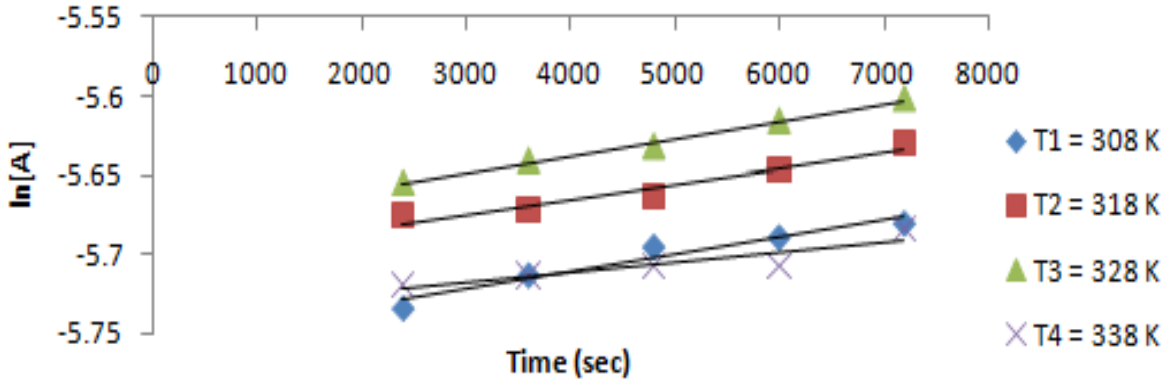

Fig. 6: Semi-log plots of Gd(III) complex yield with time at different temperatures

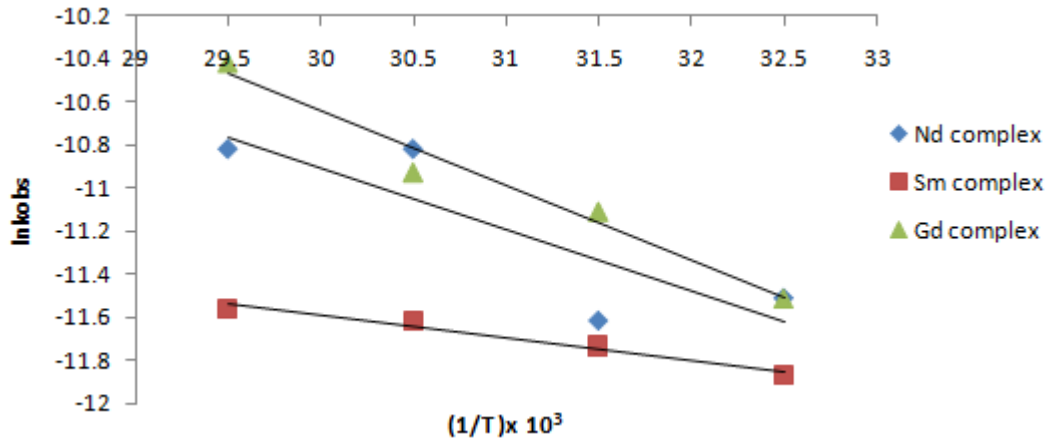

Fig. 7: Plots of lnk_{obs} versus 1/T for formation of Nd(III), Sm(III) and Gd(III) complexes

Antimicrobial analysis

The results of the zones of inhibition showed that the complexes displayed good inhibition zones. This can be explained in terms of the Tweedy's Chelation theory (Dharmaraj *et al.*, 2001). As the complexes are formed, polarities of the metal ions are reduced to a greater extent due the overlapping of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Moreover, delocalization of the π-electrons over the whole chelate is increased and lipophilicity of the complexes (Mounika *et al*., 2010). These properties now facilitate the penetration of the complexes across the membrane and DNA of the microbes leading to perturbation of the respiration process of the cell and block the synthesis of proteins, stopping further growth of the organism. Thus in extreme cases may lead to their death of the affected microbes (Xavier and Srividhya, 2014; Iniama *et al*., 2018).

Table 5: Zone of inhibition of the complexes

Compounds	S.T	E.C	S.A	A.N	T.R	C.A
Sm(III)Complex	13	10	18	NA	NA	16
Gd(III)Complex	15	11	13	NA	NA	9
Nd(III)Complex	11	12	12	NA	NA	9

S.T = *Salmonella typhi*, E.C = *Escherichia Coli*, S.A =*Staphylococcus aureus*, A.N = *Aspergillus niger;* C.A = *Candida albicans*, T.R = *Trichophytum rubbrum*; NA= No activity

Table 5: Minimum inhibitory concentration of complexes (mg/mL)

Compounds	S.T	E.C	S.A	A.N	T.R	C.A
Sm(III)Complex	12.50	25.00	6.25	NA	NA	12.50
Gd(III)Complex	25.00	25.00	12.50	NA	NA	25.00
Nd(III)Complex	25.00	25.00	25.00	NA	NA	25.00

S.T = *Salmonella typhi*, E.C = *Escherichia Coli*, S.A =*Staphylococcus aureus*, A.N = *Aspergillus niger;* C.A = *Candida albicans*, T.R = *Trichophytum rubbrum*; NA= No activity

Table 6: Minimum bacteriocidal/fungicidal concentration of the complexes (mg/mL)

Compounds	S.T	E.C	S.A	A.N	T.R	C.A
Sm	25.00	50.00	12.50	NA	NA	25.00
Gd	25.00	50.00	25.00	NA	NA	50.00
Nd	50.00	25.00	50.00	NA	NA	50.00

S.T = *Salmonella typhi*, E.C = *Escherichia Coli*, S.A =*Staphylococcus aureus*, A.N = *Aspergillus niger;* C.A = *Candida albicans*, T.R = *Trichophytum rubbrum*; NA= No activity

Zones of inhibition

Results of the zones of inhibition measured are presented on Table 5. The results of the zones of inhibition recorded showed that the complexes inhibited the growth of all the bacteria strained (*Escherichia coli, Salmonella typhi* and *Staphylococcus aureus*) used for the study. On the other hand, they could not inhibit the growth of the fungi used for the study (*Aspergillusniger* and *Trichophytonrubrum*) except *Candida albicans*. The data showed that the Sm complex gave the highest inhibition (18 mm) on the *S. aureus* strains. The Gd and Nd complexes also gave good inhibition against *S. aureus* with inhibition zones of 13 and 12 mm, respectively. On the *S. Typhi* strains, the Gd complex presented inhibition zone of 15 mm against 13 and 11 mm recorded for the Sm and Gd complexes, respectively. This result showed that the Gd complex gave better inhibition compared to Sm and Gd complexes against *S. typhi*. The Nd presented inhibition zone of 12 mm when used against the E. *coli* strains. This value was higher than that recorded for Sm and Gd (10 mm each). The growth of *C. albicans* was best inhibited by the Sm complex with zone of inhibition of 16 mm higher. This inhibition was higher than 13 and 9 mm obtained in the cases of Gd and Nd.

Minimum inhibitory concentrations (MIC)

Minimum inhibitory concentration is defined as the lowest concentration of an antimicrobial agent that can inhibit the growth of microorganisms but may or may not eliminate them (Sakhare *et al*., 2013). If it inhibits the growth and activities of bacteria without eliminating them, it is said to be a bacteriostatic agent. But if it inhibits the growth of fungi without eliminating them, it is said to be fungistatic (Sakhare *et al*., 2013). The results of the MIC recorded for the complexes are shown on Table 5. On the *S. aureus* strains, the Sm complex had the lowest MIC value of 2.25 mg/mL. Higher MIC values of 12.50 and 25.00 mg/mL were recorded for Gd and Nd complexes. This result means that the Sm with the lowest MIC value is more effective against *S. aureus* when compared to the Gd and Nd complexes. The Sm complex had MIC value of 12.50 mg/mL on *S. Typhi* and thus was higher than that of the *S. aureus* (6.25 mg/mL). On the other hand, the MICs of the Gd and Nd complexes on the *S. typhi* were 12.50 and 25.00 mg/mL respectively. These values were the same as that needed to inhibit the growth of *S. aureus*. The order of increase in strength of the complexes on the S. *typhi* was Sm>Gd<Nd. Up the as high as 25.00 mg/mL, none of the complexes could inhibit the growth of the fungi *A. niger*and *T. rubrum*. The lower MIC measured for Sm (12.50 mg/mL) against *C. albicans* implies that the Sm complex is more

effective compared to Gd and Nd complexes with MIC values of 25.00 mg/mL each.

3 Minimum bactericidal and minimum fungicidal concentration

Minimum bactericidal concentration (MBC) is the minimum concentration of an antimicrobial agent that is required to completely inhibit the bacteria strains. The minimum fungicidal concentration (MFC) is the lowest concentration need to inhibit fungi strains. The minimum bactericidal concentrations (MBC) and minimum fungicidal concentrations (MFC) were carried out to determine the smallest concentrations of the complexes that were required to inhibit the microbes completely. The smaller the value of the MBC and MFC, the more effective the sample is against the tested strains. Table 6 shows the results of the minimum bactericidal concentrations (MBC) and minimum fungicidal concentrations (MFC) of the synthesized complexes.

The lowest MBF for the *S. aureus* was presented by the Sm complex (12.50 mg/mL) while the Nd had the highest (50.00 mg/mL). The result showed that Sm complex was far more effective against *S. aureus* than the Nd complex. The minimum concentration of the Sm complex needed to inhibit *S. tyhi* was 25 mg/mL. This was far lower than the 50 mg/mL required by the Nd complex. The result means that the Nd and Gd complexes require higher dosage to inhibit the *S typhi* than the Smcomplex. High dose of the Sm and Gd complexes (50 mg/mL each) were needed to inhibit the *E. coli* while smaller dose of 25 mg/mL was needed by Nd complex. This implies that the Nd complex has more bactericidal properties than the Sm and Gd complexes. All the complexes did not show any bactericidal nor fungicidal activity even at 50 mg/mL when tested against *A. niger* and *T. rubrum.* The *C. albicans* were inhibited by just 25 mg/mL of Sm complex but required high concentration of 50 mg/mL to be inhibited when Gd and Nd complexes were used.

In general, all the MBCs and MFCs recorded showed that the Sm complex was a better anti bacterial and antifungal agent. This result agrees with the results of the MIC values obtained. On comparing the MIC, MBC and MFC values it was observed that the MBC and the MFC values were higher for almost all the microbial strains. The implication is that at the MIC values, the microbes were just bacteriostatic and fungistatic but still alive. Their growths were only inhibited but they were not eliminated. The complexes were found to be more effective on the bacteria strains than fungi strains. Since the complexes were found to be very effective on gram positive (*S. aureus*) and gram negative bacteria strains (*E. coli and S. typhi*). This is an indication that the can be for the synthesis of broad spectrum antibiotics.

Conclusion

This research work prepared Sm(III), Nd(III), and Gd(III) complexes of carbonatotetraamine. The synthesized compounds were found to be non-electrolytic, stable to heat, non-hygroscopic and monomeric in nature. From the available spectra data, octahedral geometry was proposed for the complexes. From the results of the antimicrobial analysis, it can be concluded that the compounds are potential antimicrobial agents. The study proved that Sm**(III)** complexes had the highest antimicrobial properties. The antibacterial strength displayed by the compounds showed they can be used as raw materials for synthesis of broad spectrum antibiotics.

Conflict of Interest

Authors declare that there is no conflict of interest related to this study.

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