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Thermogravimetric and Antimicrobial Properties of Some Divalent Metal Complexes of Hexamethylenetetramine

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ABSTRACT

Mn(II), Co(II), Ni(II), and Zn(II) sulphate complexes with HMTA have been synthesised and characterised by elemental analyses, melting points, IR and UV-visible spectroscopy, magnetic susceptibility and thermogravimetric analyses. The results suggest an octahedral coordination environment in which the central metal ion is covalently bonded to six aqua molecules. HMTA is bonded to the water molecules through hydrogen bonding. The complexes decompose on heating to form oxide residues. The ligand, HMTA and its metal complexes were screened in vitro for antibacterial activity against nine pathogenic bacteria strains. The activity data indicate that the metal complexes are more potent antibacterial agents than HMTA against the nine bacteria strains.

Keywords: Hexamethylenetetramine, Antimicrobial, thermogravimetric, Metal(II), Biological

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INTRODUCTION

The improper and abusive use of antimicrobial agents has resulted in many microbial infections failing to respond to antimicrobial treatment and a consequent resistance to these drugs [1-4]. Microorganisms resistant to one particular antimicrobial agent can develop resistance against others, giving rise to multidrug resistance. Amongst the bacteria of clinical importance, Staphylococcus aureus, Streptococcus pneumoniae, Enterococcus species, Pseudomonas species and Klebsiella species represent major pathogens associated with a high incidence of infections that are resistant to treatment with antibiotics [2].

Antimicrobial resistance has a significant public health and economic impact. This situation has renewed the interest of researchers, who are responding with a variety of strategies including the design and development of new antimicrobial agents with increased biological activity against the resistant pathogens [2,5-9]. Broad empirical screening of chemical compounds for antimicrobial activity represents an alternative strategy for the development of new antimicrobials [10].

Many investigations have shown that coordination of organic compounds to a metallic element causes significant changes in the biological activity of both the organic ligand and the metal [5-9, 11-14]. For example, some metal-based antibiotics such as bleomycin, streptonigrin and bastracin are more effective than the pure drugs [15]. Heterocyclic compounds do play important roles in regulating biological activities [9,12].

The ligand, hexamethylenetetramine (HMTA), is a fairly strong organic heterocyclic base (K_b = 2 x 10^{-10}) [16], possesses four potential nitrogen donor atoms. Medicinally, it has been used as an antiseptic for urinary tract infections [17]. Considering the antimicrobial properties of this ligand, research activity in our laboratories of recent, has focused on the investigation of the effect of the counter ions on the biological activity of the metal complexes of HMTA and other biologically active molecules [7-9,18,19]. In this paper, we report the synthesis, characterisation and antimicrobial properties of Mn(II), Co(II), Ni(II), and Zn(II) sulphate complexes of hexamethylenetetramine.

EXPERIMENTAL

Materials

Hexamethylenetetramine and $ZnSO_4.H_2O$ were purchased from Labosi (France) while $NiSO_4.6H_2O$, $CoSO_4.7H_2O$ and $MnSO_4.H_2O$ were purchased from Reidel-De Haen (Germany). All the chemicals were of reagent grade and were used as such without further purification. All solvents used were dried and distilled according to standard methods.

Physical Measurements

Elemental analysis for carbon, nitrogen, and hydrogen were carried out using a Carlo Erba (EA 1108) Analyser at the Technische Universität Dresden, Germany; while Mn(II), Co(II), Ni(II) and Zn(II) were estimated by complexometric titrations [20]. The melting point/ decomposition temperatures of the complexes were obtained using the Mel-Temp II Lab Device.

The infrared spectra of the ligand and complexes were recorded using pressed KBr discs in the range (4000-400 cm^{-1}) on Perkin-Elmer 457 Spectrophotometer. Electronic spectra were recorded on Hitachi U-2000 spectrophotometer.

Synthesis of the Complexes

Generally, the complexes were prepared by reaction of the respective metal salts with hexamethylenetetramine using 1:1 mole ratio, i.e. one mole of metal salt to one mole of hexamethylenetetramine.

For example, $[Ni(H_2O)_6](SO_4)(HMTA).2H_2O$ was synthesised by adding $NiSO_4.6H_2O$ (0.526 g; 2 mmol) in 40 mL of a water/ethanol solution (3:5 v/v) and the solution was heated to 50 °C while stirring. A solution of HMTA (0.28 g; 2 mmol) in 15 mL of ethanol was added dropwise to the hot solution. The mixture was further stirred for one hour at 50 °C and the resulting green precipitate was filtered and washed with diethylether and dried in vacuo over silica gel. Green crystals were obtained from the filtrate, at room temperature, after two weeks. The other complexes were similarly prepared.

Antimicrobial Tests

The antimicrobial tests were carried out in the Applied Microbiology and Molecular Pharmacology Laboratory (LMP) of the University of Yaoundé I, Cameroon.

Ten species of bacteria namely: Staphylococcus aureus (Gram-Positive bacteria), Shigella flexineri, Escherichia coli, Enterobacter cloacae, Salmonella typhi, Citrobacter freundii, Proteus vulgaris, Morganella morganii, Pseudomonas Aeroginosa and Klebsiella pneumonia (Gram-negative bacteria) were used for this study. All the species were derived from stock cultures obtained from the Medical Bacteriology Laboratory of "Centre Pasteur du Cameroun", Yaoundé, Cameroon. The microbial isolates were maintained on an agar slant at 4 ^{o}C in the Laboratory. The strains were sub-cultured on an appropriate fresh agar plate, 24 hours prior to any antibacterial tests.

Sensitivity Tests:

Sample ligand, metal salts and complexes were diluted in sterilized distilled water at 100 mg/mL. 1 mg of each test compound was placed on a sterilized filter paper disc and allowed to dry. Reference antibiotic (RA), Gentamycin was also prepared in the same manner and 10 µg placed on a sterilized filter paper disc and dried, prior to testing.

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Diffusion Tests:

In vitro antibacterial activity of the ligand, metal salts and complexes were evaluated using disc-diffusion method. Mueller-Hinton Agar was employed as microbial growth medium. The antibacterial diffusion tests were carried out as described by Berghe and Vlietink [21] using a cell suspension of about 1.5×10^6 CFU/mL obtained from the McFarland Turbidity standard N^o 0.5.

Mueller-Hinton (MH) agar was poured (to a height of 5 mm) in to sterile 9 cm diameter Petri dishes and allowed to solidify. The solid Mueller–Hinton agar were inoculated with bacteria strains using a platinum wire loop which had been previously sterilized by heating it red hot in a flame, cooled and then used for the application. The dishes were allowed to dry for 10 minutes at 37 ^{0}C in an incubator. Sterilized forceps were used for the application of the paper discs containing the test compounds on previously inoculated MH agar dishes, with that of the RA placed at the centre. The plates were kept for 30 minutes at ambient temperature to allow for pre-diffusion, and then incubated at 37 ^{0}C for 24 hours. Antimicrobial activity was evaluated by measuring the diameter of growth inhibition zone (IZ) in mm around the discs [21]. Three replicas were performed for each sample and mean values of the growth inhibition zone were calculated. Compounds were considered active when the IZ was greater than 6 mm.

RESULTS AND DISCUSSION

The physical and analytical data for the complexes are presented in Table 1. The complexes formed are crystalline solids that are air stable and non-hygroscopic as opposed to the starting salts. They are less intense in colour than the respective metal salts from which they were derived. Quality single crystals were grown from the filtrates after a week. The yields range from 62 to 82 %. Most of the complexes have a sharp melting point while some decompose within the temperature range 106 – 214 °C. A variation in colour with increasing temperature was observed for some of the complexes. This could be due to changes in the crystal structure from an octahedral to a tetrahedral environment, as water molecules are removed [22-23]. The elemental analytical results for carbon, hydrogen and nitrogen as well as the estimated metal contents are very close to the calculated values (Table 1). The results indicate that in the complexes one equivalent of the metal salt reacts with one equivalent of HMTA.

The characteristic IR band frequencies of the ligand and complexes are presented in Table 2. The very broad band centred at ca. 3400 – 3500 cm^{-1} in all the complexes indicates the O – H stretching of water. The complexes show two bands each at 1610 – 1675 cm^{-1} assigned to υ_{H2O}. The occurrence of two bands in this region indicates that there are two types of crystallographically distinct water molecules (coordinated and non-coordinated) in the complexes [16, 19, 24]. The coordination of water molecules to the cations results in the appearance of a vibrational band at 665 – 715 cm^{-1} [18, 24]. The bands at 1238 and 805 cm^{-1} which have been assigned to $\upsilon_{(C-N)}$ and $\rho_{(CH2)}$, respectively for the free ligand indicate that HMTA

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is not coordinated to the metal ions and is found outside the coordination sphere. The strong absorption band at 1160 – 1180 cm^{-1} is due to the sulphate ion [26]. The sulphate ions and HMTA molecule are likely to form hydrogen bonds with coordinated and uncoordinated water molecules [16].

Table 1: Physical and Analytical Data of the Complexes

Complex	Colour	Melting Point/˚C	%Yield	Elemental Analyses: % Found (% Calculated)				
				%M	%C	%H	%N	
$[Mn(H_2O)_6](SO_4)(HMTA).2H_2O$	Dirty-white	214	64	12.72 (12.62)	16.38 (16.55)	6.29 (6.48)	12.64 (12.87)	
$[Co(H_2O)_6](SO_4)HMTA).2H_2O$	Violet	106	73	13.42 (13.45)	16.40 (16.26)	5.97 (6.01)	12.70 (12.76)	
$[Ni(H_2O)_6](SO_4)$ (HMTA).$2H_2O$	Green	117	62	13.37 (13.52)	16.60 (16.41)	5.97 (6.02)	12.65 (12.76)	
$[Zn(H_2O)_6](SO_4)$ (HMTA).$2H_2O$	White	203	82	14.56 (14.67)	15.97 (16.16)	6.00 (5.88)	12.38 (12.57)	

Table 2: Relevant IR Absorption Bands (cm^{-1}) of HMTA and its Complexes

Complex	$\upsilon_{(O-H)}$	υ_{H2O}	$\upsilon_{s(C-N)}$	υ_{SO4}^{2-}	$\rho_{(CH2)}$	υ_{M-O}
HMTA			1238s		810s	
$[Mn(H_2O)_6](HMTA)(SO_4).2H_2O$	3400br	1635m 1610m	1235s	1160w	805m	682m
$[Co(H_2O)_6](HMTA)(SO_4).2H_2O$	3400br	1675m 1625w	1236s	1165wr	810w	690m
$[Ni(H_2O)_6](HMTA)(SO_4).2H_2O$	3395br	1655m 1610w	1235s	1180m	800br	685w
$[Zn(H_2O)_6](HMTA)(SO_4).2H_2O$	3500br	1645m 1615w	1235m	1180s	800w	715m

br = broad; s = sharp; m = medium; w = weak

The electronic spectral data for the complexes are summarised in Table 3. The effective magnetic moment of 6.06 B.M. for the manganese(II) complex is close to the literature value of 5.92 B.M. for high spin octahedral Mn(II) complexes [27,28]. The electronic spectrum for this complex was not obtained due to its almost colourless nature (d^5). The electronic spectrum of the cobalt(II) complex reveals two bands at 20,620 cm^{-1} and 19,230 cm^{-1} which have been assigned to $^4T_{1g}(F)$, $^4T_{1g}(P)$ and $^4T_{1g}(F)$, $^4A_{2g}$ transitions, respectively. Similar bands have been reported in literature [19,22,29] suggesting an octahedral geometry around the cobalt(II) ion. The effective magnetic moment of $[Co(H_2O)_6](SO_4)(HMTA).2H_2O$ is 4.81 B.M. This value is higher than the spin-only moment of 3.87 BM due to large orbital contribution for an octahedral cobalt(II) ion with a $^4T_{1g}$ ground term [28]. The electronic spectrum of the nickel(II) complex exhibits a band around 25,000 cm^{-1} and a second broad and split band at 14,500 – 13,700 cm^{-1}. These bands have been assigned to $^3A_{2g}$, $^3T_{1g}(P)$ and $^3A_{2g}$, $^3T_{1g}(F)$ transitions, respectively [30]. The ratio 1.72 of the height of the first to that of the second band, indicates an octahedral environment around the nickel(II) ion [31]. The room temperature magnetic

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moment of the nickel(II) complex is 3.76 B.M. which is close to the values obtained for octahedral nickel(II) ion halide HMTA complexes [22]. The zinc complex is found to be diamagnetic as expected.

Table 3: Magnetic and Visible Spectral Data of the Complexes

Compound	μ_{eff} (BM)	υ_{max} x 10^3 cm^{-1} (ϵ)	Assignment
$[Mn(H_2O)_6](SO_4)(HMTA).2H_2O$	6.06		
$[Co(H_2O)_6](SO_4)(HMTA).2H_2O$	4.81	20.62 (5.6)	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		19.23 (7.8)	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$
$[Ni(H_2O)_6](SO_4)(HMTA).2H_2O$	3.76	25.00 (8.2)	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
		14.50 (3.0)	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		13.70 (3.1)	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
$[Zn(H_2O)_6](SO_4)(HMTA).2H_2O$	0.20		

Thermogravimetric Analysis

Thermogravimetric analytical data for the complexes are presented in Table 4. The Thermogravimetric analyses (TGA-DTA) of the compounds generally showed the occurrence of three consecutive processes, namely dehydration, ligand pyrolysis and inorganic residue formation.

Table 4: Thermal Data for the Nickel and Zinc Complexes

Complex	Step	TGA		DTA	
		Temp. Range /°C	Decomposition /%	Peak Temp. /°C	Nature
$[Ni(H_2O)_6](HMTA)(SO_4).2H_2O$	I	40 – 170	30.7	108	Endothermic
	II	180 – 330	21.7	495	Exothermic
	III	340 – 420	10.5		
	IV	430 – 470	9.9		
	V	470 – 480	2.5		
	VI	480 – 540	4.0		
	VII	550 – 750	3.1		
$[Zn(H_2O)_6](HMTA)(SO_4).2H_2O$	I	50 – 120	30.4	90	Endothermic
	II	120 – 210	10.2	656	Exothermic
	III	210 – 240	3.9	193	Endothermic
	IV	250 – 315	6.2	534	Exothermic
	V	320 – 570	20.6		
	VI	570 – 700	10.2		

The TGA thermogram for $[Ni(H_2O)_6](HMTA)(SO_4).2H_2O$ (Figure 1) showed a weight loss from 60 °C to 170 °C. This weight loss corresponds to ca. 31% of the initial sample weight consistent with the loss of eight water molecules. The anhydrous compound formed starts decomposing at 200 °C, with intermittent slow and fast rates of decomposition, until it ends at 750 °C. The rapid weight loss equivalent to 22 % and 33 % corresponds to the departure of the sulphate ion and HMTA molecule in the form of a mixture of gases. A residue (~ 17 %) is formed which is in good agreement with the 17.1 % calculated for the metal oxide NiO.

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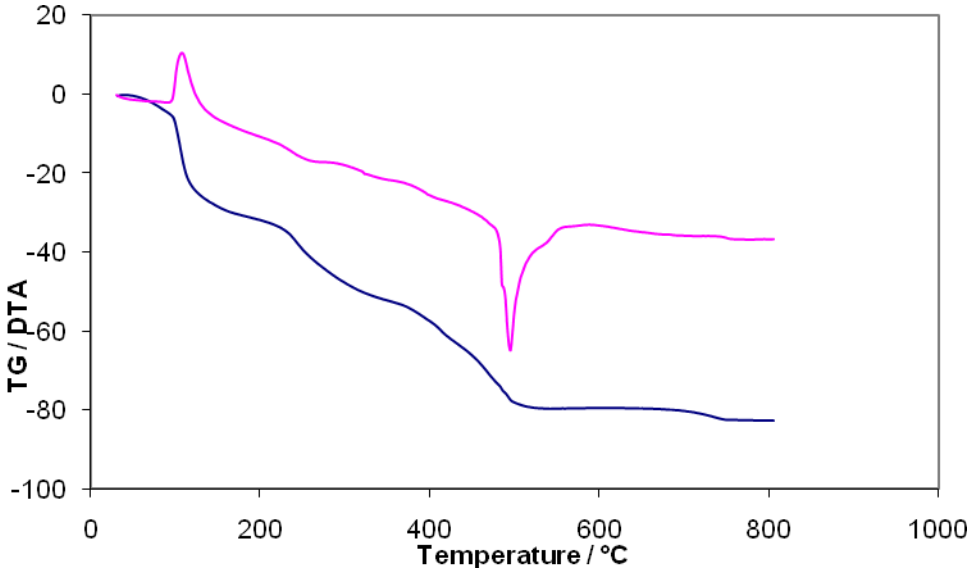

Figure 1: TGA and DTA Plots for $[Ni(H_2O)_6](SO_4)(HMTA).2H_2O$

The DTA curve for $[Ni(H_2O)_6](hmt)(SO_4).2H_2O$ shows an endothermic peak at 108 °C corresponding to the loss of water molecules and an exothermic peak at 495 °C corresponding to the loss of the sulphate ion and HMTA molecules alongside the formation of nickel oxide.

TGA curve for the zinc complex $[Zn(H_2O)_6](HMTA)(SO_4).2H_2O$ (Figure 2) shows that it starts losing water molecules at 50 °C and becomes completely deaquated at 120 °C. The total weight loss in the first two steps (~ 30 %) corresponds to the loss of eight water molecules per formula unit. On further heating, the compound starts decomposing at 210 °C and a residue of zinc oxide is formed.

Endothermic peaks at 90°C and 193°C in the DTA curve of $[Zn(H_2O)_6](HMTA)(SO_4).2H_2O$ correspond to the removal of water molecules. The exothermic peaks at 534 °C and 650 °C correspond to the loss of the sulphate ion and HMTA molecule with the formation of an oxide residue. The anhydrous residues obtained on deaquation do not reabsorb any water molecules from the atmosphere suggesting that the framework structures break down once the water molecules are lost [32].

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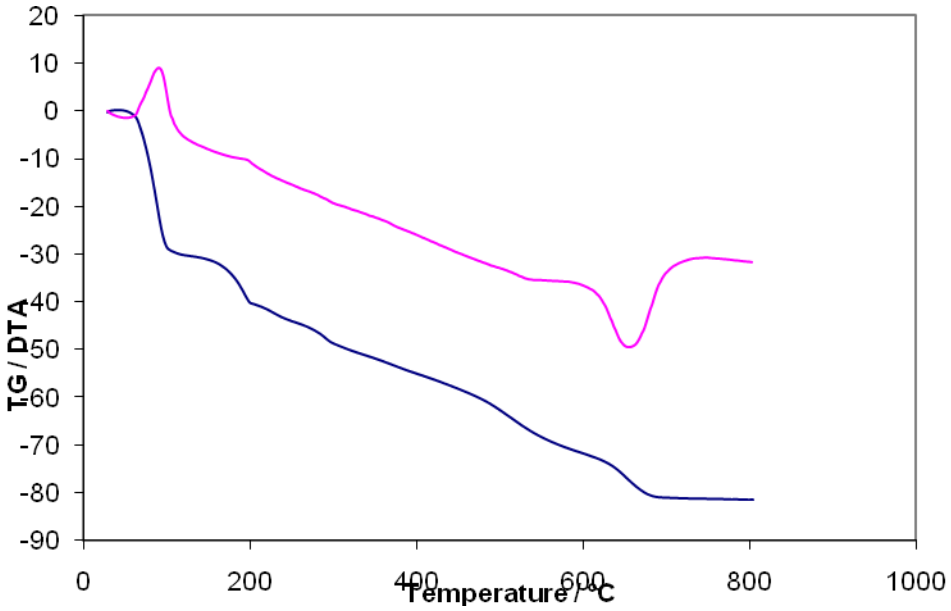

Figure 2: TGA and DTA Analysis of $[Zn(H_2O)_6](SO_4)(HMTA).2H_2O$

Antimicrobial Screening

The susceptibility of the bacteria strains towards the different compounds, judged by measuring the diameter of the growth inhibition zone, is presented in Table 5. The higher the diameter of the inhibition zone (IZ) the more active the compound. HMTA was found to be active only against one (S. typhi) of the nine pathogens while the metal complexes showed increased activity against all the pathogens. This indicates that metal ions do play an important role in enhancing the antimicrobial activity of the ligand on interaction with it. This increase in activity could be due to the reduction of the polarity of the metal ion by partial sharing of the positive charge with the ligand's donor atoms so that there is electron delocalisation within the metal complex. This may increase the lipophilic character of the metal chelate, enabling it to permeate the lipid layer of the organism killing them more effectively [33,34].

Table 5: Inhibition Zone of the Complexes against Tested Bacterial Strains

Complex	A	B	C	D	E	F	G	H	I
HMTA	-	-	-	-	7	-	-	-	-
$[Mn(H_2O)_6](HMTA)(SO_4).2H_2O$	-	-	13	-	-	14	-	-	-
$[Co(H_2O)_6](HMTA)(SO_4).2H_2O$	14	21	19	24	18	21	21	17	20
$[Ni(H_2O)_6](HMTA)(SO_4).2H_2O$	-	14	23	19	13	19	15	16	-
$[Zn(H_2O)_6](HMTA)(SO_4).2H_2O$	16	24	20	13	16	18	19	16	17
Reference Antibiotic	19	22	27	24	23	23	23	23	22

A = S. aureus; **B** = E. chloacae; **C** = S. flexneri; **D** = E. coli; **E** = S. typhi;
F = M. morganii; G = P. aeruginosa; H = C. freundi; **I** = P. vulgaris;

The pathogens S. flexneri and M. morganii were inhibited by all the complexes. The manganese(II) complex was the least active of the tested compounds while the cobalt(II) and zinc(II) complexes were the most active, having higher IZ values for most of the bacteria strains tested. The complexes can be arranged in decreasing order of activity as: $[Co(H_2O)_6](HMTA)(SO_4).2H_2O$ > $[Zn(H_2O)_6](HMTA)(SO_4).2H_2O$ > $[Ni(H_2O)_6](HMTA)(SO_4).2H_2O$ > $[Mn(H_2O)_6](HMTA)(SO_4).2H_2O$. It was observed that the zinc(II) complex showed a higher activity against E. chloacae than the reference antibiotic(R.A). The high antibacterial activity of the cobalt(II) and zinc(II) complexes could be further explored.

CONCLUSION

Manganese(II), cobalt(II), nickel(II) and zinc(II) sulphate complexes with HMTA as ligand have been synthesised and characterised by elemental, IR, UV-vis, room temperature magnetic moment and thermogravimetric analyses. The IR absorption bands observed in the spectra suggest that HMTA is not coordinated to the metal centres. The electronic spectra of the complexes indicate that they have high-spin octahedral geometries around the metal centres with six water molecules covalently bonded to it. The observed effective magnetic moments further corroborate the structural arrangement. The complexes all undergo decomposition in more than one step and the TGA curves show that the processes dehydration, ligand pyrolysis and inorganic residue formation occur consecutively. Antibacterial studies of these complexes against nine bacteria species indicate that there is an increase in activity of the ligand on coordination to the metal ion. The cobalt(II) and zinc(II) complexes were the most active. The order of activity of the complexes is $[Co(H_2O)_6](HMTA)(SO_4).2H_2O$ > $[Zn(H_2O)_6](HMTA)(SO_4).2H_2O$ > $[Ni(H_2O)_6](HMTA)(SO_4).2H_2O$ > $[Mn(H_2O)_6](HMTA)(SO_4).2H_2O$. The higher activity of the cobalt(II) and zinc(II) complexes could be further explored to increase their spectrum of activity.

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