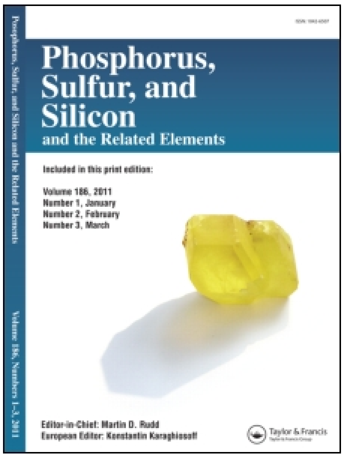

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Sulfur-Bonded Coordination Compounds of Palladium(II) and Platinum(II) and Their Antimicrobial Activity

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The synthetic, spectroscopic, and biological studies of some new palladium(II) and platinum(II) complexes derived from biologically active sulfur donor ligands 1H-indol-2,3-dione benzothiazoline (Bzt_1H) and 5-nitro-1H-indol-2,3-dione benzothiazoline (Bzt_2H) have been described. The reactions were carried out in 1:2 molar ratios. The authenticity of the benzothiazolines and their complexes has been established on the basis of elemental analyses; molecular weight determinations; and IR, ^1H NMR, ^{13}C NMR, and UV spectral studies. Based on IR and ^1H NMR spectral studies, a square-planar structure has been assigned to these complexes. Studies were conducted to assess the comparative growth inhibiting potential of the synthesized complexes against the benzothiazolines for a variety of fungal and bacterial strains. The studies demonstrate that the ligands and complexes possess antimicrobial properties. Further, it was noted that the growth-inhibiting potential of the complexes is greater than the parent benzothiazolines.

Keywords Antimicrobial activity; benzothiazolines; Pd(II) and Pt(II) complexes; spectral studies

INTRODUCTION

Interest in metal complexes of sulfur–nitrogen chelating agents synthesized from thiosemicarbazide,[1] ^{4}N-substituted thiosemicarbazide,[2] S-alkyl esters of dithiocarbazic acid,[3] and 2-aminobenzenethiol[4] has been stimulated by their interesting physicochemical properties and potentially useful pharmacological properties.[5] Metal chelates of these ligands have also been used as pesticides and fungicides in agriculture.[6] The inherent biological potential of sulfur donor ligands prompted us to

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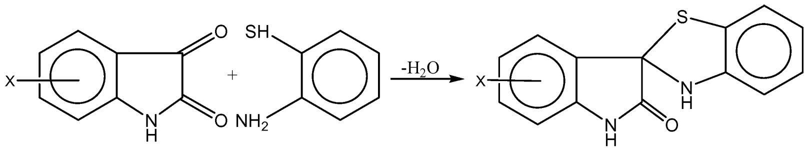
undertake systematic studies with transition metals, as these possess antimicrobial,[7] antifertility,[8] and antitumor activities.[9] It has been well established that certain platinum and palladium complexes[10] are of biological importance due to their carcinostatic activity and interest in biological chemistry.[11] Platinum metal and its complexes are widely used as catalysts.[12] Palladium complexes with some Schiff base ligands derived from S-alkyl esters of dithiocarbazic acid have been found to exhibit marked anticancer activity against leukemia.[13] Antimicrobial aspects and antifertility activity of coordination compounds of palladium(II) and platinum(II) have also been reported in recent years.[14,15] In addition to their potential bioactivity, palladium(II) complexes of some nitrogen/sulfur-containing ligands have also been shown to act as catalysts for selective hydrogenation of terminal alkynes to generate corresponding alkenes.[16] In view of the importance of palladium(II) and platinum(II) complexes in chemotherapy as well as in catalysis, and as part of our continuing interest in metal-Schiff base complexes, we report herein the preparation, characterization, and evaluation of biological activity of some Pd(II) and Pt(II) complexes derived from two monofunctional bidentate benzothiazolines, Bzt_1H and Bzt_2H.

MATERIALS AND METHODS

Palladium and platinum salts, $PdCl_2$ and $PtCl_2$, as well as isatin and o-aminithiophenol were purchased from Lancaster and used as such. 5-Nitroisatin was prepared in the laboratory by the method in the literature.[17] All the solvents were dried and distilled before use. Molecular weights were determined by the Rast camphor method. Chlorine was estimated by Volhard's method. Pd(II) and Pt(II) were estimated gravimetrically. Nitrogen was estimated by Kjeldahl's method, and sulfur was estimated by Messenger's method.[18] Conductivity measurements were made with a Systronics model 305 conductivity bridge. The electronic spectra were recorded on a Varian–Cary/2390 spectrophotometer at RSIC, I.I.T., Chennai. Infrared spectra of the ligands and their complexes were recorded with the help of a Nicolet Megna FTIR-550 spectrophotometer on KBr pellets. ^{13}C NMR and ^{1}H NMR spectra were recorded on a JEOL-AL-300 FT NMR spectrometer in DMSO-$d_6$using TMS as the internal standard.

Preparation of Sulfur Donor Ligands, Benzothiazolines

The benzothiazolines were prepared by the condensation of 1H-indol-2,3-dione and 5-nitro-1H-indol-2,3-dione with 2-mercaptoaniline in 1:1



Where, X = H (Bzt_1H) and 5-Nitro (Bzt_2H)

FIGURE 1 Synthesis of the ligands.

molar ratio in ethanol (Figure 1). The reaction mixture was stirred for 3–4 h, and the resulting product was filtered off, recrystallized from ethanol, and dried in vacuum.

Their physicochemical properties and analytical data are given in Table I.

Preparation of $[Pd(Bzt)_2]$ Type of Complexes

The methanolic solution of $PdCl_2$ was mixed with methanolic solution of benzothiazolines in 1:2 molar ratios. Aqueous NH_4OH was added dropwise to the reaction mixture until it was weakly alkaline

TABLE I Analytical Data and Physical Properties of the Ligands and Their Complexes

Compound and Empirical Formula	Color and Mp (°C)	Yield (%)	Found (Calcd.) (%) N	S	Cl	M	Mol. Wt. Found (Calcd.)
Bzt_1H	Yellow	89	10.84	12.10	—	—	235.15
($C_{14}H_{10}N_3O_3S$)	126–128		(11.01)	(12.61)			(254.31)
Bzt_2H ($C_{14}H_{10}N_2OSCl$)	Parrot green	85	13.91	10.16	—	—	286.13
	152–155		(14.04)	(10.71)			(299.30)
$[Pd(Bzt_1H)_2]Cl_2$	Brown	75	8.03	9.23	10.13	15.28	628.42
($[Pd(C_{14}H_{10}N_3O_3S)_2]Cl_2$)	155–158		(8.16)	(9.34)	(10.33)	(15.51)	(685.92)
$[Pd(Bzt_1)_2]$	Brown	69	9.01	10.23	—	17.13	556.3
($[Pd(C_{14}H_9N_3O_3S)_2]$)	207–210		(9.13)	(10.46)		(17.29)	(613.99)
$[Pd(Bzt_2H)_2]Cl_2$	Brick red	78	10.56	8.12	9.02	13.26	642.23
($[Pd(C_{14}H_{10}N_2OSCl)_2]Cl_2$)	152–155		(10.83)	(8.26)	(9.13)	(13.71)	(775.90)
$[Pd(Bzt_2)_2]$	Brown	75	11.45	9.02	—	15.13	672.36
($[Pd(C_{14}H_9N_2OSCl)_2]$)	170–172		(11.95)	(9.12)		(15.31)	(702.98)
$[Pt(Bzt_1H)_2]Cl_2$	Army green	68	7.09	8.14	9.09	24.98	732.45
($[Pt(C_{14}H_{10}N_3O_3S)_2]Cl_2$)	138–142		(7.23)	(8.27)	(9.15)	(25.18)	(774.60)
$[Pt(Bzt_1)_2]$	Green	62	7.56	8.99	—	27.49	669.85
($[Pt(C_{14}H_9N_3O_3S)_2]$)	136–138		(7.98)	(9.13)		(27.80)	(701.67)
$[Pt(Bzt_2H)_2]Cl_2$	Green	72	9.25	7.23	8.12	22.16	845.54
($[Pt(C_{14}H_{10}N_2OSCl)_2]Cl_2$)	160–164		(9.72)	(7.41)	(8.20)	(22.56)	(864.59)
$[Pt(Bzt_2)_2]$	Black	70	10.26	9.09	—	24.49	755.45
($[Pt(C_{14}H_9N_2OSCl)_2]$)	178–180		(10.61)	(8.10)		(24.64)	(791.67)

(pH ca. 8.0). The mixture was then heated under reflux for about 1 h. Upon cooling, the complexes were separated out, filtered, washed with methanol, and dried in vacuum.

Preparation of $[Pd(BztH)_2]Cl_2$ Type of Complexes

The methanolic solution of $PdCl_2$was mixed with methanolic solution of benzothiazolines in 1:2 molar ratios. The mixture was stirred on a magnetic stirrer for 2–3 h in the presence of a few drops of concentrated HCl. The resulting products were recovered by filtration, washed with methanol, and dried in vacuum.

Preparation of $[Pt(Bzt)_2]$ Type of Complexes

These complexes were prepared by dissolving $PtCl_2$ in ethanol and then adding an ethanolic solution of benzothiazolines to this solution in 1:2 molar ratios. Aqueous NH_4OH was added dropwise to the reaction mixture until it was weakly alkaline (pH ca. 8.0). The reaction mixture was heated under reflux for about 1 h. Upon cooling, the complexes were separated out, filtered, washed with ethanol, and dried in vacuum.

Preparation of $[Pt(BztH)_2]Cl_2$ Type of Complexes

The ethanolic solution of $PtCl_2$ was mixed with an ethanolic solution of benzothiazolines in 1:2 molar ratios. The mixture was stirred on a magnetic stirrer for 2–3 h in the presence of a few drops of concentrated HCl. The resulting products were recovered by filtration, washed with ethanol, and dried in vacuum.

The physicohemical properties and analytical data of these complexes are listed in Table I.

Antifungal Activity

The antifungal activity was evaluated against *Fusarium oxysporum* and *Macrophomina phaseolina* using Czapek's agar medium having the composition glucose 20 g, starch 20 g, agar-agar 20 g, and distilled water 1000 mL. To this medium was added the requisite amount of the compounds after being dissolved in dimethylformamide so as to obtain three different concentrations (50, 100, and 200 ppm). The medium then was poured into Petri plates, and the spores of fungi were placed on the medium with the help of an inoculums needle. These Petri plates were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at 30 ± 2°C. The controls were also run, and three replicates were used in each case. The linear growth of the fungus was recorded by measuring the diameter of the fungal colony after 96 h, and the percentage inhibition was calculated by the following equation:

$$\% \text{ Inhibition} = (\text{C} - \text{T})100/\text{C}$$

Where, C and T are the diameters of the fungal colony in the control and the test plates, respectively.[19]

Antibacterial Activity

Antibacterial activity was tested against *Klebsiella aerogenous* and *Bacillus substilis* using the paper disc plate method.[20] The nutrient agar medium (peptone, beef extract, NaCl, and agar-agar) and 5 mm diameter paper discs of Whatman filter paper No.1 were used. The compounds were dissolved in methanol for obtaining the concentrations of 500 and 1000 ppm. The filter paper discs were soaked in these solutions, dried, and then placed in the Petri plates previously seeded with the test organisms. The plates were incubated for 24 h at 28 ± 2°C, and the inhibition zone around each disc was measured.

RESULTS AND DISCUSSION

The reactions of the above benzothiazolines with $PdCl_2$ and $PtCl_2$ have been carried out in 1:2 molar ratios in methanol and in 1:1 water and ethanol solutions, respectively. The metal chloride interacts with the ligands in presence of few drops of concentrated HCl to form complexes of the type $[M(BztH)_2]Cl_2$. However, complexes of the type $[M(Bzt)_2]$ were obtained when reactions were carried out in the presence of aqueous NH_4OH:

$$MCl_2 + 2BztH \rightarrow [M(BztH)_2Cl_2]$$

$$MCl_2 + 2BztH + 2NH_4OH \rightarrow [M(Bzt)_2] + 2NH_4Cl + 2H_2O$$

Where, M = Pd(II) and Pt(II) and BztH is the benzothiazoline molecule

The reactions proceed easily, and all the complexes are soluble in DMSO, DMF, and $CHCl_3$. The molar conductance values of 10^{-3} M solutions of $[M(Bzt)_2]$ type of complexes lie in the range 10–15 ohm^{-1} cm^2 mol^{-1} in dry DMF indicating their nonelectrolytic behavior. However, the $[M(BztH)_2]Cl_2$ type of complexes are 1:2 electrolytes, with conductance values of 206–225 ohm^{-1} cm^2 mol^{-1}. The complexes are monomers as revealed by their molecular weight determinations.

TABLE II Electronic Spectral Data (nm) of Palladium(II) and Platinum(II) Complexes

Complexes	Transition	λ_{max} (nm)	Abs.	ε (M^{-1} cm^{-1})
$[Pd(Bzt_1H)_2]Cl_2$	$^1A_{1g} \to {}^1A_{2g}(\nu_1)$	460	0.05272	5272
	$^1A_{1g} \to {}^1B_{1g}(\nu_2)$	403	0.07075	7075
	$^1A_{1g} \to {}^1E_{1g}(\nu_3)$	375	0.07989	7989
$[Pd(Bzt_1)_2]$	$^1A_{1g} \to {}^1A_{2g}(\nu_1)$	463	0.05122	5122
	$^1A_{1g} \to {}^1B_{1g}(\nu_2)$	415	0.06791	6791
	$^1A_{1g} \to {}^1E_{1g}(\nu_3)$	378	0.07813	7813
$[Pt(Bzt_2H)_2]Cl_2$	$^1A_{1g} \to {}^1A_{2g}(\nu_1)$	520	0.04947	4947
	$^1A_{1g} \to {}^1B_{1g}(\nu_2)$	419	0.05785	5785
	$^1A_{1g} \to {}^1E_{1g}(\nu_3)$	344	0.10334	10334
$[Pt(Bzt_2)_2]$	$^1A_{1g} \to {}^1A_{2g}(\nu_1)$	523	0.04953	4953
	$^1A_{1g} \to {}^1B_{1g}(\nu_2)$	418	0.05785	5785
	$^1A_{1g} \to {}^1E_{1g}(\nu_3)$	340	0.11150	11150

$l = 1$ cm; c = 10^{-5} M.

Electronic Spectra

The electronic spectra of the complexes were recorded in distilled DMSO. The spectra of the complexes show three bands due to three d–d spin allowed transitions. These are corresponding to the transitions from the three lower-lying d orbitals to the empty $d_{x^2-y^2}$ orbital. The ground state is $^1A_{1g}$ and excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$, and $^1E_{1g}$ in order of increasing energy. Three d–d transition bands are observed in the regions, 460–523, 403–419, and 340–378 nm (Table II). These bands are attributed to $^1A_{1g} \to {}^1A_{2g}$, $^1A_{1g} \to {}^1B_{1g}$, and $^1A_{1g} \to {}^1E_{1g}$ transitions, respectively. The electronic spectra of these complexes indicate the square planar geometry.[21] The value of molar extinction coefficient (ε) for each transition shown by the complexes is also calculated by the Beer Lambert's law, i.e., $\varepsilon = A/cl$, where $l = 1$ cm and $c = 10^{-5}$ M.

IR Spectra

In the IR spectra of the free benzothiazolines (Bzt_1H) and (Bzt_2H), the –NH stretching and deformation bands appear at 3350–3250 cm^{-1} and 1675–1700 cm^{-1}, respectively. The absence of the v(SH) band at 2600–2500 cm^{-1} and $v(C = N)$ band at 1620–1600 cm^{-1} is strong evidence for the existence of benzothiazoline structure rather than the Schiff base structure.[22] In the spectra of metal complexes, the v(NH) bands disappear, suggesting the deprotonation of the ligands on chelation. A strong and sharp band in the region 1600–1620 cm^{-1} ascribed to$\nu(C=N)$, is observed in the metal complexes, confirming that the ligands adopt the Schiff base form in complexes. In the case of $[M(BztH)_2]Cl_2$ type of complexes, bands due toν(SH) at 2500–2520 cm^{-1} are observed. However, no ν(M-Cl) band[23] in the region 295–340 cm^{-1} is observed in the spectra of $[M(BztH)_2]Cl_2$ type of complexes, suggesting that chloride is ionic in these complexes. The appearance of the non-ligand bands further supports the coordination of the ligands to the metals through the azomethine nitrogen and thio sulfur atoms. It is known that the cis form of such type of complexes give rise to two ν(M-N) bands, whereas the trans complexes give rise to only one IR active ν(M-N) band. The presence of only one ν(M-N) band in the present case suggests that the complexes exists in the trans form.[24]

^{1}H NMR Spectra

The ^{1}H NMR spectra of the free Bzt_1H and Bzt_2H and their metal derivatives were recorded in DMSO-d_6. The signals at δ5.52 and 4.25 ppm are assigned to the –NH protons. These signals disappear in the metal complexes, indicating the deprotonation of this functional group on complexation (Table III). In the $[M(BztH)_2]Cl_2$ type of complexes, the signals appearing at δ4.51–5.50 ppm are due to the SH proton, and these are not observed in $[M(Bzt)_2]$ type of complexes. The free ligands show a complex multiplet at δ6.65–8.74 ppm for the aromatic protons, and it remains more or less at the same position in the spectra of the complexes.

TABLE III ^{1}H NMR Spectral Data (δ, ppm) of the Ligands and Their Corresponding Complexes

Compound	–NH (Ring) (bs)	–NH (Free) (bs)	–SH (bs)	Aromatic protons (m)
Bzt_1H	11.92	5.52	–	6.70–8.74
Bzt_2H	12.02	4.25	–	6.65–7.20
$[Pd(Bzt_1H)_2]Cl_2$	11.98	–	4.51	6.74–8.02
$[Pd(Bzt_1)_2]$	11.61	–	–	6.72–8.00
$[Pt(Bzt_2H)_2]Cl_2$	11.23	–	5.50	6.78–8.09
$[Pt(Bzt_2)_2]$	11.02	–	–	6.50–8.00

bs = broad signal; m = multiplet.

TABLE IV ^{13}C NMR Spectral Data (δ, ppm) of the Ligands and Their Corresponding Complexes

Compound	$>\overset{\vert}{\mathrm{C}}\text{—N/C=N}$ carbon	Thiolo carbon	Aromatic carbons
Bzt_1H	162.70	150.52	140.26, 130.39, 129.68, 134.58, 125.23, 127.10
Bzt_2H	169.82	160.23	142.23, 129.23, 132.17, 135.15, 132.74, 131.23
$[Pd(Bzt_1H)_2]Cl_2$	167.19	164.77	147.15, 144.39, 140.68, 131.58, 125.67, 126.13
$[Pd(Bzt_1)_2]$	164.57	169.14	145.16, 143.34, 139.66, 130.56, 124.67, 127.12
$[Pt(Bzt_2H)_2]Cl_2$	170.42	174.35	148.17, 145.49, 141.65, 132.54, 126.63, 128.11
$[Pt(Bzt_2)_2]$	171.15	170.13	147.15, 144.39, 140.68, 131.58, 125.67, 126.13

^{13}C NMR Spectra

^{13}C NMR spectra of benzothiazolines and corresponding metal complexes were also recorded in dry DMSO, and assigned peak positions are listed in Table IV. The noticeable shift in the position of carbon attached to azomethine nitrogen and thiolic sulfur in the spectra of metal complexes confirms the inferences drawn earlier on the basis of IR and ^{1}H NMR spectra concerning the participation of nitrogen and sulfur in bonding with metal atoms.

On the basis of the foregoing discussion, the structures shown in Figures 2 and 3 have been proposed for the complexes.

Antimicrobial Activity

Antimicrobial activity of the synthesized ligands and their corresponding metal complexes on selected fungi, *Fusarium oxysporum* and *Macrophomina phaseolina*, and two bacteria, *Klebsiella aerogenous* and

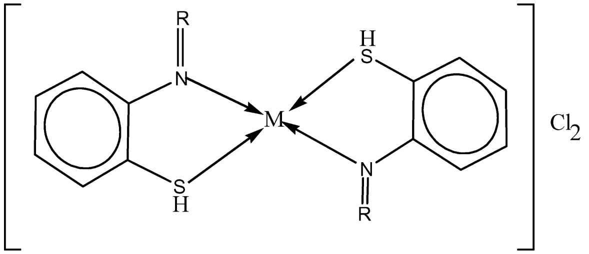
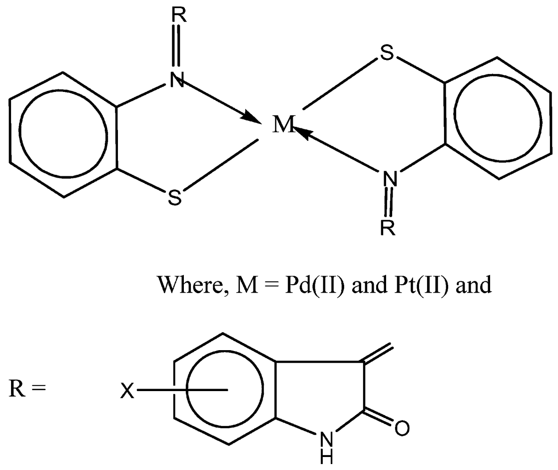


FIGURE 2 Addition complex.



Where, M = Pd(II) and Pt(II) and

X= H (Bzt_1H) and 5-Nitro (Bzt_2H)

FIGURE 3 Substitution complex.

Bacillus substilis, were carried out. The action of the ligands and their complexes as fungicides against pathogenic fungi and as bactericides against bacteria are recorded in Tables V and VI, respectively. The results showed that the ligands alone were quite toxic but their activity

TABLE V Antifungal Screening Data for the Ligands and Their Complexes

	(%) Inhibition after 96 h (Conc. in ppm)					
	Fusarium oxysporum			*Macrophomina phaseolina*		
Compound	50	100	200	50	100	200
Bzt_1H	40	55	67	30	45	60
Bzt_2H	33	37	48	27	32	53
$[Pd(Bzt_1H)_2]Cl_2$	47	57	63	47	59	64
$[Pd(Bzt_1)_2]$	45	56	61	52	60	65
$[Pd(Bzt_2H)_2]Cl_2$	41	48	56	50	58	65
$[Pd(Bzt_2)_2]$	40	45	53	50	68	61
$[Pt(Bzt_1H)_2]Cl_2$	55	66	69	52	59	63
$[Pt(Bzt_1)_2]$	53	60	66	52	58	64
$[Pt(Bzt_2H)_2]Cl_2$	41	46	53	48	57	53
$[Pt(Bzt_2)_2]$	40	45	52	50	58	61
Flucanazole	82	100	100	86	100	100

TABLE VI Antibacterial Screening Data for the Ligands and Their Complexes

	Diameter (mm) of inhibition zone after 24 h (Conc. in ppm)			
	Klebsiella aerogenous		*Bacillus substilis*	
Compound	500	1000	500	1000
Bzt_1H	4	6	5	7
Bzt_2H	6	8	4	6
$[Pd(Bzt_1H)_2]Cl_2$	9	11	7	10
$[Pd(Bzt_1)_2]$	9	10	10	12
$[Pd(Bzt_2H)_2]Cl_2$	10	13	11	13
$[Pd(Bzt_2)_2]$	12	13	11	12
$[Pt(Bzt_1H)_2]Cl_2$	12	14	12	13
$[Pt(Bzt_1)_2]$	11	13	11	12
$[Pt(Bzt_2H)_2]Cl_2$	10	14	12	13
$[Pt(Bzt_2)_2]$	11	13	11	12
Tetracyclin	16	18	15	18

increased on complexation. The activity of the complexes is thought to be enhanced due to the introduction of the metal ions in the ligands.[25] The chelation increases the lipophilic nature of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane. It may be postulated that these compounds deactivate various cellular enzymes that play a vital role in different metabolic pathways of these microorganisms. It has also been proposed that the ultimate action of the toxicant is the denaturation of one or more proteins of the cell, depending on which normal cellular processes are impaired.[26]

CONCLUSION

On the basis of the analytical data and spectral studies, it has been observed that the ligands originally exist in benzothiazoline form and later on are converted into Schiff base form and coordinated to the metal atoms in a monobasic bidentate manner, and thus possess square planar geometry. The complexes showed better antimicrobial activities as compared to the parent ligands. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased.

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