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SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL EVALUATION OF NOVEL $TL^{(I)}$-18C6/DB18C6 COMPLEXES

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ABSTRACT
The affinity of crown ethers for a metal ion is strongly dependent on the size of the ring of the crown ether. The crown ether-metal ion binding is enhanced in the absence of non-coplanar donor oxygen atoms and electron withdrawing substituents in the crown ether skeleton. The present paper describes preparation, spectral characterization and antimicrobial studies of novel $Tl^{(I)}$-18C6/db18C6 complexes. The metal salts used for complexation were salts of nitrophenols. Products were isolated from thallium salts of all the three monoionic ligands, 2-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol. The bonding patterns of complexes were suggested from the studies of elemental analysis, molar conductivity, FTIR, UV-Vis and ^{1}H-NMR spectral analysis. Antibacterial and antifungal activities of the synthesized complexes were measured by Kirby Bauer disc diffusion method.

KEYWORDS: 18C6, DB18C6, ONPH, DNPH, TNPH.

INTRODUCTION
Coordination chemistry of macrocyclic ligands has been a fascinating area of current research interest to the inorganic chemists all over the world. The continued interest and quest in designing new macrocyclic ligands stem mainly from their use as models for protein-metal binding sites in a substantial array of metalloproteins in biological systems, as synthetic ionophores, as models to study the magnetic exchange phenomena, as therapeutic reagents in chelate therapy for the treatment of metal intoxication, as cyclic antibiotics that owe their antibiotic actions to specific metal complexation, to study the guest-host Interactions, in solvent extraction and separation of various ions[1-11], stabilize the low oxidation states of various elements and in catalysis.[12,13] These macrocycles which contain varying combinations of aza, oxa, phospha, and sulfa ligating atoms can be tailored to accommodate specific metal ions by the fine tuning of the ligand design features, such as the macrocyclic hole size, nature of the ligand donors, donor set, donor array, ligand conjugation, ligand substitution, number and sizes of the chelate rings, ligand flexibility, and nature of the ligand backbone.[14-18] Crown ethers form complexes with a host of cations, including alkali, alkaline earth, heavy metals, lanthanides and transition metals.[19-29] The different types of macrocyclic ligands are particularly exciting because of the importance in generating new areas of fundamental chemistry and many opportunities of applied chemistry. The majority of macrocycles represent creative and focused efforts to design molecules which will have particular uses.

Heavy metal cations are very toxic and the highly selective complexation by macrocyclic ligands which may remove only these harmful cations and not affecting the levels of biologically important ones is of fundamental interest and of potential practical importance.[30,31] Interest in synthesis and designing of new macrocyclic ligands is also due to their potential use in biological systems: as synthetic ionophores, as therapeutic reagents for the treatment of metal intoxication, as cyclic antibiotics, to study the biological guest-host interactions.[32-38] Five types of pathogenic bacteria and one fungi were used in this work which includes four gram positive bacteria, Staphylococcus aureus, E. faecalis, lactobacillus, B. subtilis, one gram negative bacteria Escherichia coli and one fungi C. albicans. These fungi and bacteria are known for its resistance to most of the developed antibiotics and is known to be the major cause of many health issues and infections.[39-41]

MATERIALS AND METHODS
Chemicals used were of S. Aldrich / E. Merck, A.R. grade. The metal contents were estimated by flame photometric method. The melting point of the synthesized compounds, were determined by electrical tempo T-1150 apparatus. Molar conductivities of the

compounds were measured using Systronic conductivity meter-306 at concentration 10^{-3} M in methanol at 30(±0.5)^{0}C. FTIR spectra were recorded by Perkin Elmer RX1 (4000-450 cm^{-1}). UV-visible spectral data were recorded through Systronic double beam spectrophotometer-2203 (600-200 nm). The ^{1}H−NMR spectra of ligand and crown ether complexes were recorded in $CDCl_3$ by Bruker DRX-300.

EXPERIMENTAL

Preparation of thallium salt of nitrophenols; Tl.ONP, Tl.DNP and Tl.TNP

About 0.02 mol of appropriate nitrophenol was taken in a conical flask and dissolved in 50 ml of dry ethanol with constant stirring with the help of glass rod. Further 0.02 mol of metal hydroxide was dissolved in ethanol and was slowly added to the alcoholic solution of nitrophenol with constant stirring. The mixture was continuously refluxed on hot plate with stirring for 50 minutes at 78^{0}C. After that, the solution was corked and kept standed. On cooling this solution solid crystalline product began to precipitate slowly. Product was filtered, washed with absolute ethanol and dried in an electric oven at 80^{0}C.

Preparation of 18C6 and dibenzo18C6 ether

Preparation of crown ethers which work as a strong complexing host molecule was one of the important part of this research work. These were prepared by the synthetic methods as reported in literature.[42,43]

Table 1: Physical properties of thallium salts.

Compound	Molecular Formula	Colour	Melting point (^{0}C)
Tl.ONP	$C_{16}H_{24}NO_8Tl$	Light yellow	275 d
Tl.DNP	$C_{16}H_{23}N_2O_{10}Tl$	Bright yellow	270 d
Tl.TNP	$C_{16}H_{22}N_3O_{12}Tl$	Light orange	270 e

d – decomposition temp, e – explosion temp

Preparation of adduct of 18-crown-6 ether with thallium salts of 2-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol

The dried organic salt (0.002 mol) was suspended in 50 ml dry methanol and heated it with constant stirring to get a clear solution. Stoichiometric proportion of 18-crown-6 ether (0.528 gm, 0.002 mol) of was added to this solution. This reaction mixture was refluxed on a hot plate equipped with magnetic stirrer at 50-55^{0}C. A clear solution was formed. It was filtered and concentrated to half of its bulk. On cooling this solution, solid crystalline product began to precipitate. The product was separated and allowed to stand overnight then filtered on a buchner funnel. The compound was washed with a little cold dry methanol and dried over KOH desiccator.

18C6.Tl(ONP) : $C_{18}H_{28}NO_9Tl$; 1604, 1501, 1354, 1250, 1020, 875, 763, 562, 533

18C6.Tl(DNP) : $C_{18}H_{27}N_2O_{11}Tl$; 1601, 1448, 1356, 1220, 1018, 860, 768, 528

18C6.Tl(TNP) : $C_{18}H_{26}N_3O_{13}Tl$; 1631, 1471, 1353, 1249, 1108, 836, 767, 584, 524

Similarly, for the preparation of adducts of dibenzo18-crown-6 with thallium salts, same amount of appropriate dried thallium salt was refluxed with 0.72 gm (0.002 mol, 0.72 gm) of dibenzo 18-crown-6 ether.

DB18C6.Tl(DNP) : $C_{26}H_{27}N_2O_{11}Tl$; 1626, 1435, 1325, 1219, 1130, 870, 772, 590, 570, 529

DB18C6.Tl(TNP) : $C_{26}H_{26}N_3O_{13}Tl$; 1631, 1454, 1363, 1215, 1057, 845, 766, 580, 530, 475

Mechanism of Complexation

In most cases, metal cation-crown ether complexation processes can be explained by the multistep Eigen-Winkler mechanism.

$Tl(Pic) + L \rightarrow [Tl^+.L](Pic^-)$

Where, Tl^+ = solvated metal ion, L = free macrocyclic ligand, $Tl^+.L$= solvent-separated metal-macrocyclic ligand pair, $(Tl.L)^+$ = complex with metal cation embedded in the macrocyclic cavity.

Micrrobial Assay and Suspensions

Five bacterial isolates Escherichia coli, Staphylococcus aureus, E. faecalis, B. subtilis, Lactobacillus and one fungal isolate of C. albicans were used in this work. The isolates were planted on the surface of an agar on petriplates incubated at 37°C for 24 hrs and stored at 4°C for the later use. The bacterial suspensions were prepared by transferring a colony from each bacterial isolate using a metal loop into test tubes containing liquid nutrient broth and were incubated at 37°C for 18 hrs.

The Antibacterial Test of the Prepared Complexes

An amount of 18-20 ml of freshly prepared solid nutrient agar was transferred to sterilized glass petridishes in sterilized environment (inside the biological safety cabinets; Laminar air flow) and left to cool and solidify. 0.1 ml from each bacterial suspension was transferred to the dishes containing the solidified nutrient agar and was uniformly inoculated. The streaking was done in at least three directions over the surface of the agar to obtain uniform growth, and final sweep was made around the rim of the agar. The plates were allowed to stand for 5 minutes to dry, after that four to five wells with a diameter of 0.6 mm were made in each dish using a sterile borer.

Table 2: Prominent IR bands of thallium complexes (in cm^{-1}).

Compound	ν_{as} (C–O–C)	ν_1 (–NO_2), ν_3 (–NO_2)	ν (C–H) Phenolic out of Plane	ν_s(C–H)$_{bending}$, ν_{as}(–CH_2–)$_{bending}$	ν(N=O)$_{str}$ in C–NO_2	ν(M–O) / ν(M–O_{crown})
18C6.Tl(ONP)	1020	1604, 875	763	1501, 1354	1250	533, 562
18C6.Tl(DNP)	1018	1601, 860	768	1448, 1356	1220	528
18C6.Tl(TNP)	1108	1631, 836	767	1471, 1353	1249	524, 584
DB18C6.Tl(DNP)	1130	1626, 870	772	1435, 1325	1219	529, 570, 590
DB18C6.Tl(TNP)	1057	1631, 845	766	1454, 1363	1215	475, 530, 580

RESULT AND DISCUSSION

UV-Visible study

UV-visible absorption spectra of synthesized compounds provide significant evidence of bonding in complexes. Saturated crown ethers do not show any absorption above 220 nm. Synthesized complexes shows only some deviation of π - π*, n - π*, σ - π* and σ - σ* transitions due to shifting of electron density from donor atoms to cationic species. The slight change in spectral band position is usually taken as either solvent effect or interaction of electron cloud of donor atom of ligand with thallium ion. The bond energy in organic compound possess energy equivalent to absorption energy of ultraviolet or visible radiation as they form bonds by ion-dipole interactions and/or involvement of non-bonding electrons with central metal ions.[44-46] The n - σ* transition of phenolic (C–O) group is observed at high energy and phenyl ring π - π*, σ - σ* transitions between 180–260 nm region. Besides bonding electronic transitions, intermolecular transition known as charge transfers (C–T) transitions of high intensity are also observed in synthesized complexes.[47,48]

FTIR study

The free nitro groups of nitrophenols display $\nu(-NO_2)_{as}$ and $\nu(-NO_2)_s$ stretching around 1620±15 cm^{-1}, 1260±30 cm^{-1}. The –NO_2 bending band is located at 840±15 cm^{-1} which has been shifted to lower frequency by 10–15 cm^{-1} on bond formation.[49] The phenyl group in all nitrophenols display phenyl (C=C) and (C–H) skeletal vibration at different positions in finger print region. The phenyl group skeletal vibrations are observed at 1590–1620 cm^{-1}, 1510±15 cm^{-1} and 1280±10 cm^{-1}. The IR band observed near 740–780 cm^{-1} is attributed to phenyl ring (C−H) out of plane bending band. The absorption at about 1110 cm^{-1} is attributed to phenolic (C–O) stretching band. In present study all nitrophenols display ν(O–H) frequency as broad band in the region 3140–3320 cm^{-1} and ν(C–O) near 1120±10 cm^{-1}.[50,51] The ν(O–H) disappears in thallium salts and ν(C–O) band shifted to higher frequency due to acquiring higher C–O bond order. This increase is attributed to bonding of phenolic oxygens in all complexes.

The stretching bands of –NO_2 in Tl.ONP), Tl.DNP and Tl.TNP is at around 1605 cm^{-1}, 1620±2 cm^{-1} and 1640–1645 cm^{-1}. These vibrations shifted to lower frequency in complexes. The crown ethers display $\nu(CH_2)$ stretching vibrations at 2925±10 cm^{-1} and these are little affected on bonding with metal ions. The crown ethers in uncoordinated state display ν(C-O-C) stretching vibration band near 1115±10 cm^{-1}. This ν(C-O-C) vibration band shifted to lower frequency by 10 to 60 cm^{-1} in almost all compounds suggesting involvement of crown ether oxygen in bond formation with thallium ion. Some complexes are hygroscopic in nature and thus their IR spectrum displays a broad band of water molecules around 3350–3420 cm^{-1}, with maxima near 3405±10 cm^{-1}. In the far-IR region new bands, absent in the spectrum of the free ligands, are found in the 425-590 cm^{-1} region, which may be assigned to the $\nu(M–O_{crown})$ stretching frequency.[52-54] Thus IR studies of complexes unambiguously suggest bonding of thallium salts with crown ethers.

^{1}H-NMR Study

Information on some crown ether interactions leading to supramolecule formation is available from detailed measurements of the chemical shift variations of protons of the crown ethers as a function of concentration of the metal ion with the crown ether.[55] The conformation and the binding of small-ring dibenzo crown ethers with small cations in solution have been previously investigated.[56] The ^{1}H-NMR study of synthesized crown ether complexes provides useful information regarding structure of complexes.[57]

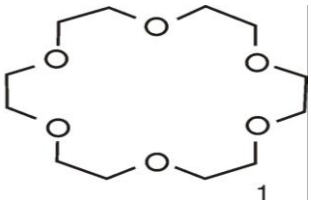

Figure 1: 18-crown-6.

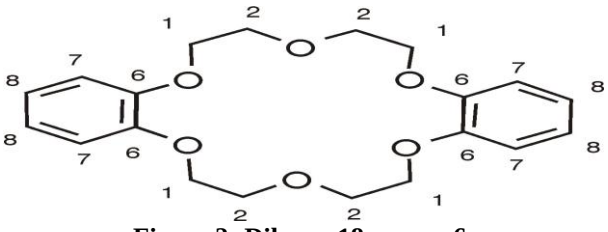

Figure 2: Dibenzo18-crown-6.

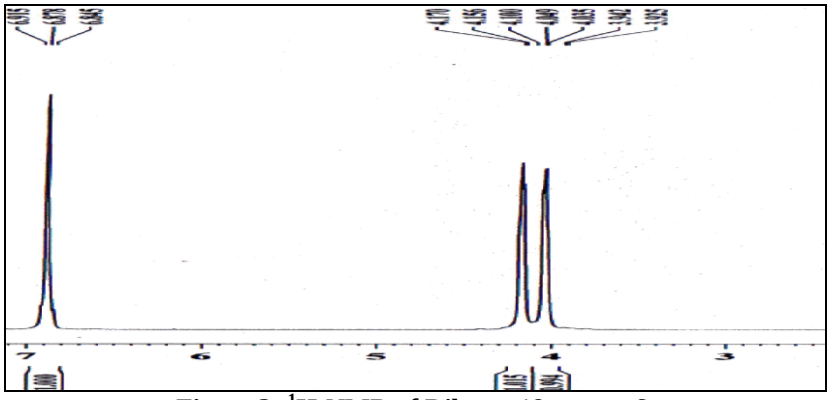

Figure 3: ^{1}H-NMR of Dibenzo18-crown-6.

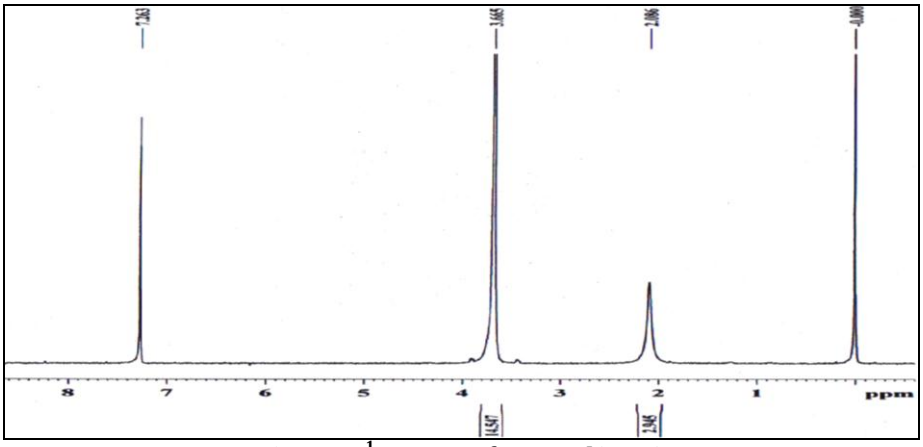

Figure 4: ^{1}H-NMR of 18C6.Tl(TNP)

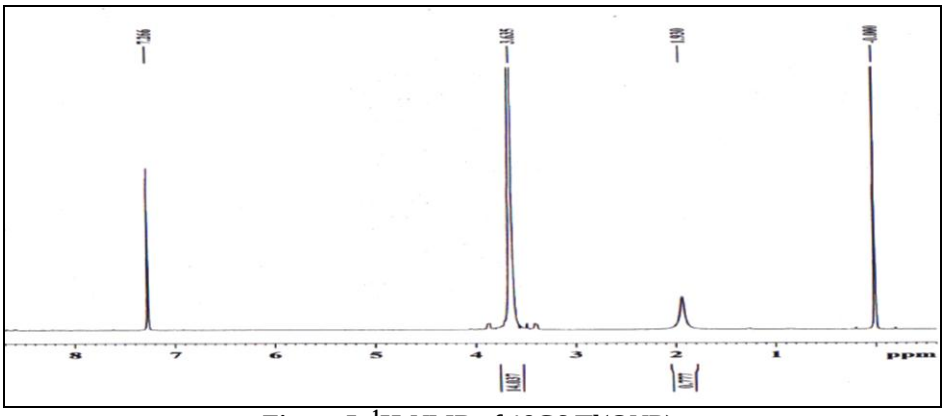

Figure 5: ^{1}H-NMR of 18C6.Tl(ONP).

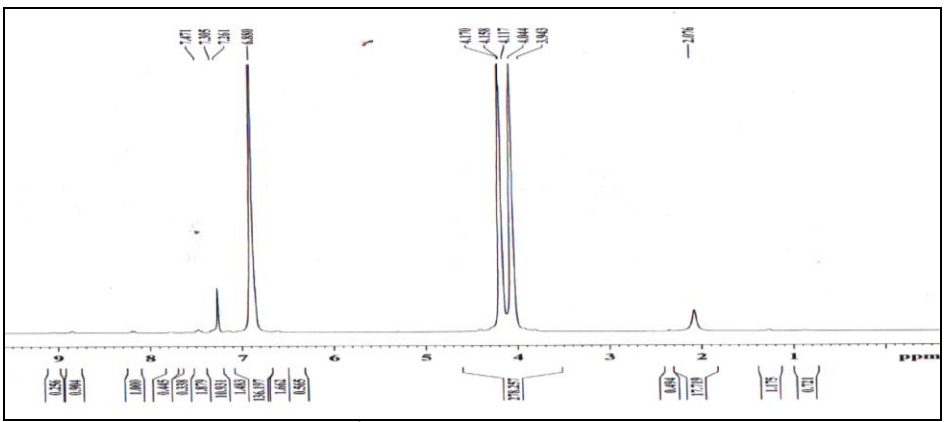

Figure 6: ^{1}H-NMR of DB18C6.Tl(DNP).

Table 3: ^{1}H-NMR Chemical shift (δ) for free crown ethers and synthesized complexes.

Compound	δ(1H)	δ(2H)	δ(7H, 8H)
18C6	3.623		
Tl^+-18C6	3.665		
DB18C6	3.925	4.035	6.8 − 7.0
Tl^+-DB18C6	3.943	4.031	6.8 − 7.0

Small changes were observed in the chemical shift of 1H in 18C6 and 1H as well as 2H in dibenzo18C6, which moved downfield upon complexation. Possible reasons for this downfield shift are the conformational change in the macrocyclic skeleton which could affect the electron density through the Fermi contact term.[58] Significant change in the –OCCO– dihedral angle upon complexation is probably a major contributor to the chemical shift in some complexes. The chemical shift variation indicates a possible change in the structure and/or electronic environment of 1H and 2H in these macrocyclic systems on complexation. After formation of the $[Tl^+.L](Pic^-)$ complex, the proton chemical shift of δ(–CH_2–O–) shows significant downfield shifts [Δδ(–CH_2–O–) = 0.08-0.25 ppm], indicating metal-ligand bond formation.[59-61] The relative change in the downfield shift shows the relative strength of the synthesized complexes.[62,63] Coordination of macrocyclic ether with metal ion provides information regarding change of electron shielding effect, spin-spin coupling, spin-spin splitting pattern and extent of coupling constant(j).

The proton NMR spectrum of dibenzene18C6 polyether shows ^{1}H-NMR peaks δ = 3.9–4.1 ppm, (16H, 8 –CH_2O–), δ = 6.8–7.0 ppm (8H, aryl –CH–)[64-67] in $CDCl_3$. The shift of –CH_2– signals in complexes from free crown ether suggests the coordination of crown ether oxygen of 18C6 as well as dibenzo18C6 with thallium ion. Since the nature of ^{1}H-NMR peaks are almost similar thus, spectrum of only one compound is shown. Figure-4 shows proposed structures of complexes $[Tl^+.L](Pic^-)$, where M = Tl^+, L = 18C6/db18C6 and OX = ONP^-/ DNP^-/TNP^- based on all reported evidences.

Crown ethers have many applications in catalysis, organic synthesis, biochemistry, microbiology, and material science. Their applications in biology include the ability to regulate enzyme activity, interact with DNA, and act as antimicrobial agents. Simple crown compounds such as 15C5 and db18C6 have the ability to interact with enzymes. Antimicrobial test was performed using Kirby Bauer disc diffusion method.[68,69] Five bacterial isolates, Escherichia coli, Staphylococcus aureus, E. faecalis, B. Subtilis, Lactobacillus and one fungal isolate of C. albicans were used in this work. The isolates were planted on the surface of an agar on petriplates incubated at 37°C for 24 hrs and stored at 4°C for the later use. Stericle filter paper dishes are placed in 4-5 places on the petriplates. The test compound was then added at the centre of each paper. The plates are inverted and then incubated for 16 hrs. After incubation depending on the strain and chemical complex inhibition zones were developed around each test sample. The diameter of the zone of inhibition around each disc were measured to the nearest millimeter.[70,71] Controlled experiments were performed and only equivalent volume of solvents were applied on the paper discs. The antimicrobial activities were expressed as minimum inhibitory concentration (MICS) values[72,73] corresponding to the lowest concentration of the compound that produces a measureable zone of inhibition. Table shows the inhibition zones of the prepared complexes. All the prepared complexes gave good inhibition zones. All the used ligands showed very less activity against the tested bacteria and fungi while all the prepared complexes showed very good results. Results of antimicrobial tests of synthesized complexes are listed in table-4.

Antimicrobial evaluation of the prepared complexes

Table 4: Antimicrobial activity of synthesized complexes.

Compound	Antibacterial activity										Antifungal activity	
	Gram Positive								Gram Negative			
	S.aureus		E.faecalis		B.substillis		Lactobacillus		E.coli		C.albicans	
	1 mg	2mg	1 mg	2mg	1 mg	2 mg	1 mg	2 mg	1 mg	2 mg	1 mg	2mg
$[Tl^+.18C8].(ONP^-)$	-	-	--	--	-	-	-	--	-	-	+	+
$[Tl^+.18C6].(DNP^-)$	+	+	-	-	+	-	+	+	-	-	-	--
$[Tl^+.18C6].(TNP^-)$	--	--	--	--	-	-	-	--	-	-	-	-
$[Tl^+.db18C6].(DNP^-)$	+	+	-	-	+	-	-	+	-	-	+	+
$[Tl^+.db18C6].(TNP^-)$	--	--	--	--	-	-	-	--	-	-	-	-

--Very active - Moderately active + Not active

Phenolic compounds destabilizes the outer membrane of bacteria and fungi making it more easy for the complexes to pass through the bacterial membrane.[74-76] From data of table 4, it can be seen that the $[Tl^+.18C6].(TNP^-)$ and $[Tl^+.db18C6].(TNP^-)$ possesses modest but net antibacterial activity against the two bacteria species, S.

aureus and E. faecalis used in experiments, whereas the metal complexe $[Tl^{+}.18C6].(ONP^{-})$ acts moderately effective against S. aureus, B. substillis and E. coli, but much less efficient against C. albicans as compared to $[Tl^{+}.18C6].(TNP^{-})$. Activity of $Tl^{(I)}$-18C6 complexes against Lactobacillus and activity of $Tl^{(I)}$-db18C6 complexes against E. coli has been shown in percentage inhibition vs. average activity with time graph in figure 10 and figure 11.

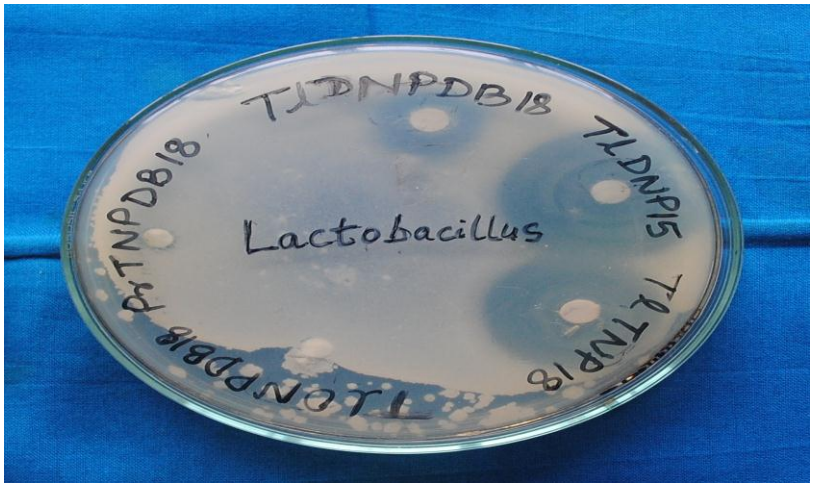

Figure 7: Microbial study against Lactobacillus.

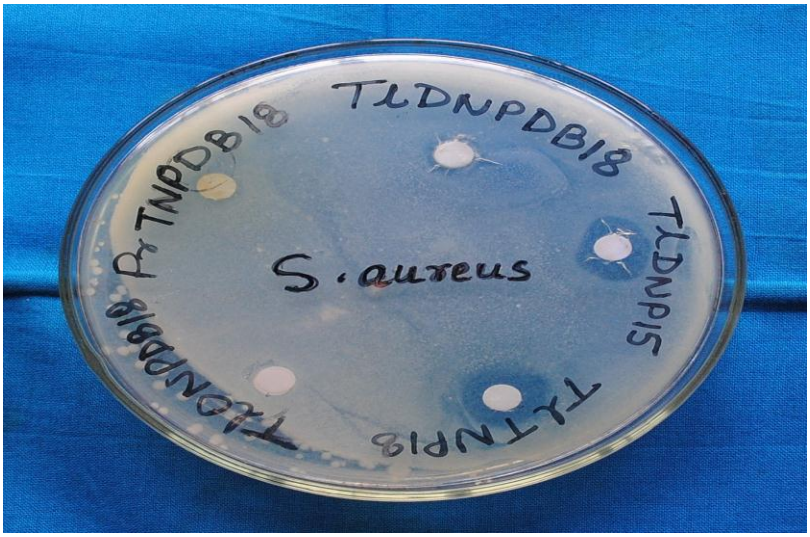

Figure 8: Microbial study against S. aureus.

Figure 9: Microbial study against E. coli.

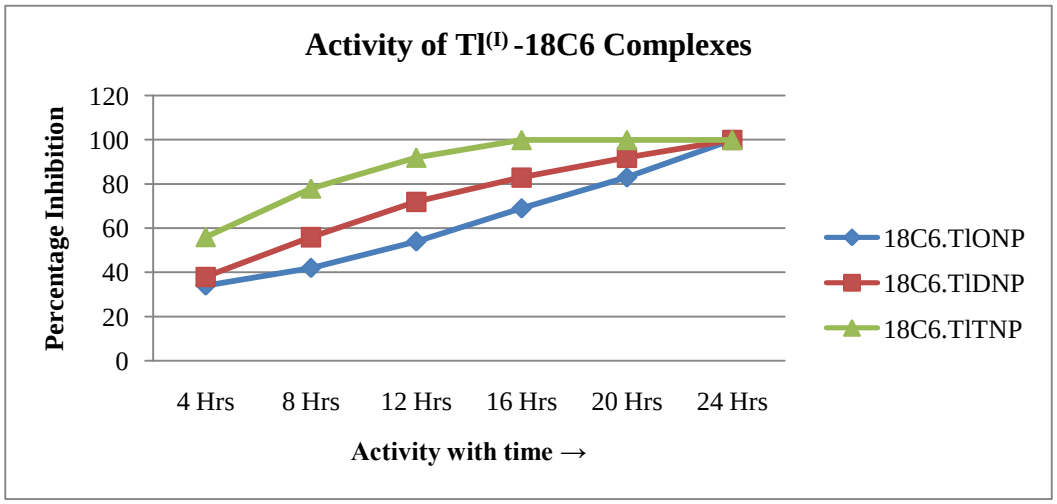

Figure 10: Activity of $Tl^{(I)}$-18C6 complexes against Lactobacillus with time.

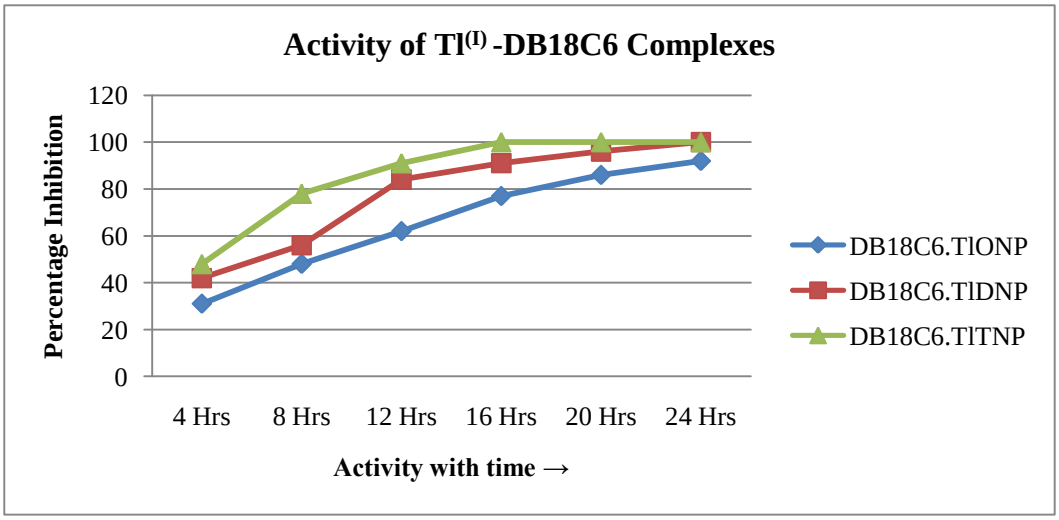

Figure 11: Activity of $Tl^{(I)}$-DB18C6 complexes against E. coli with time.

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