

# Selected Alkaline Earth Metal Chelates with 1,8-Dihydroxyanthraquinone: Synthesis, Characterization, Catalytic and Antimicrobial Study

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**Abstract :** The ligand is versatile in forming a series of chelates with alkaline earth metal ions such as Mg(II), Ca(II) and Sr(II). The ligand and metal chelates were characterized by IR, elemental analysis, molar conductance, UV-Visible, Mass and TGA spectral studies. The spectral studies indicated that the ligand was coordinated to the metal ions in neutral tridentate fashion through two of the oxygen atoms in the phenolic ring with deprotonation and one of the oxygen atom of carbonyl group of anthraquinone structure. Thermal decomposition of chelates were also examined. The catalytic study of all the chelates in organic synthesis reaction was carried out. The chemical kinetic reactions were also studied to check the effect of chelates on rate of reaction. The ligand and metal chelates were screened for their antimicrobial activities.

**Index Terms -** Alkaline earth metals, Antimicrobial activities, catalytic study

## I. INTRODUCTION

1,8-dihydroxyanthraquinone, also known as chrysazin or Dantron, is an organic substance, formally derived from anthraquinone by the substitution of two hydrogen atoms by hydroxyl groups (–OH). It is used in some countries as a stimulant laxative[1]. Dantron is discovered in several species of plants and insects. It has been isolated from dried leaves and stems of *Xyris semifuscata* harvested in Madagascar, and roots of *Da Huang*, a Chinese traditional herbal medicine. Dantron also appears to be biosynthesized by some insects. The presence of dantron in insects may be a way of protection from predators[2]. Dantron has been prepared by several processes, including the alkaline hydrolysis of 1,8-dinitroanthraquinone, the caustic fusion of 1,8-anthraquinone-disulfonic acid, the diazotization of 1,8-diaminoanthraquinone followed by hydrolysis of the bisdiazido compound, the acid hydrolysis of 1,8-dimethoxyanthraquinone in glacial acetic acid-sulfuric acid, the alkaline hydrolysis of 1,8-anthraquinone disulfonic acid using calcium oxide, and the reaction of 1,8-dinitroanthraquinone with sodium formate or potassium formate[3]. In 1987, US manufacturers voluntarily withdrew production of all human drug products containing dantron [4]. Dantron is synthesized in the Federal Republic of Germany, India, Japan, Poland, the UK and the USA[5]. Dantron has been widely used since the beginning of this century as a laxative and as an intermediate for dyes [1,6]. Dantron was tested for carcinogenicity by oral administration in single studies in male mice of one strain and in male rats of one strain. In mice, a small increase in the incidence of hepatocellular carcinomas and a large increase in adenomatous polypoid hyperplasia of the colon were observed; there was also an increased combined incidence of adenomas and adenocarcinomas of the colon and caecum. In rats, dantron increased the incidence of adenocarcinomas of the colon. In one study, dantron caused chromosomal aberrations in human lymphocytes in vitro. It gave contradictory results with respect to the induction of unscheduled DNA synthesis in rodent cells and was mutagenic to yeast in one study and to *Salmonella typhimurium*. Dantron did not inhibit gap-junctional intercellular communication in human cells, but conflicting results were obtained in Chinese hamster cells. Metal chelates have an extensive range of medicinal applications. A number of metallic elements play vital roles in biology and it is clear that many organic compounds used in medicine require metal ions for activation or biotransformation to achieve their mode of action, consequently[7]. Metal ions are often classified as ‘toxic’ and ‘non-toxic’, yet their biological activity depends very much on speciation and it is now widely accepted that, with carefully controlled coordination chemistry, even ‘toxic’ metals can exhibit therapeutic properties.[8] It is therefore very significant to explore and understand the effects of varying the oxidation state, numbers and geometries of coordinated ligands on the biological properties of metal chelates to design metal – based drugs.

## II. EXPERIMENTAL

Kinetic data for the formation of complexes are obtained by various methods. The complex formation of ML from metal ion,  $M^{n+}$ , and ligand L, can be described in terms of a rapid pre-equilibrium. The formation rate is affected by electron configuration and oxidation state of  $M^{n+}$ .

### 2.1. Material and methods

Analytical grade chemicals were used throughout the course of experimental work. Spectroscopic grade solvents were employed for recording the spectra. The compound 1,8-dihydroxy anthraquinone (Sigma Aldrich) was used as the ligand. All metal carbonates used were also A.R. grade. A definite volume of 70% HClO<sub>4</sub> was diluted with water to obtain 0.2M perchloric acid solution. The exact strength was determined by pH metric titration against standard 0.2M NaOH solution. 125 ml 0.2 M perchloric acid was taken and solid metal carbonate was added in it till effervescences observed (slight excess addition was done). The solution was stirred for 30 minutes and filtered and thus 0.1M metal perchlorate in aqueous solution was obtained.

The metal perchlorate solution thus obtained was standardized using EDTA solution[9]. Then 100ml metal perchlorate solution was taken in round bottom flask. The metal perchlorate was very cautiously heated until almost dryness. then 100ml ethyl alcohol

was added in it. Then 0.1M Dantron in chloroform was used as a ligand. The synthesis of complex was carried out by mixing 100ml 0.1M metal perchlorate solution and 100ml 0.1M ligand alcoholic solution. The mole ratio of ligand and metal was (1 : 1). The reaction mixture was refluxed for 3 hours at ~ 70°C temperature. After three hours the reaction mixture was cooled. The complex slowly precipitated, The complex, thus obtained, was washed well with absolute alcohol and water to remove unreacted metal salt and ligand. All the complexes were dried at room temperature.

## 2.2. Analysis and physical measurements

Melting point and TLC (solvent: Toluene: methanol: water in 1: 1: 1 ml ratio) was carried out for the ligand and complexes. The conductance were recorded on a Zeal Tech conductometer (Cell constant  $1 \pm 10\% \text{ cm}^{-1}$ ). The molar conductance was measured by using  $1 \times 10^{-3} \text{ M}$  solutions of metal chelates prepared in DMF solvent. Microanalysis for carbon and hydrogen were measured by using THERMO FINNIGAN CHNS analyzer of Flash EA 112 series (Italy). The percentage proportions of Mg(II), Ca(II) and Sr(II) were determined by EDTA titration method[10]. Complexes were decomposed with a mixture of concentrated sulphuric acid and nitric acid in 1:1 ml ratio. Metal content of complexes were obtained by complexometric titration against standard EDTA sodium salt solution using Eriochrome black T as an indicator at proper pH value. The pH of the solution was maintained by using ammonia ammonium chloride buffer solution[11,12,13]. Electronic spectra of complexes were obtained on UV-1800, Shimadzu (double beam) UV-Vis Spectrophotometer. Chemical kinetics study for redox reactions and catalytic study for reductive coupling reaction were carried out. The minimum inhibition concentrations for complexes were determined by Broth dilution methods to evaluate the antimicrobial activities of the synthesized complexes[14]. The IR spectra were recorded on a Shimadzu spectrophotometer. TGA Analyses were carried out by Mettler star SW 8.10(room temperature to  $1400^\circ\text{C}$ ). The ligand 1,8-dihydroxyanthraquinone is abbreviated as DNTR and the chelates of Mg(II), Ca(II) and Sr(II) are abbreviated as Mg.DNTR, Ca.DNTR and Sr.DNTR.

**Table 1: Physical characterization of 1,8-dihydroxyanthraquinone ligand and its complexes**

Chelates	Molecular weight Gm/mole	$\frac{R_f}{\text{Value M.P } ^\circ\text{c}}$	Colour $\lambda_{\text{max}}$ (nm)	Molar Conductivity Milli mho/cm % Yield	% Metal Found % Metal Calculated	% Carbon found calculated	% Hydrogen found calculated
DNTR	240.211	$\frac{0.88}{191}$	Orange Brown 209,402	$\frac{8.04}{---$	---	---	---
Mg.DNTR	280.5172	$\frac{0.89}{188}$	Reddish Brown 212,419	$\frac{9.01}{14.40}$	$\frac{8.05}{9.08}$	$\frac{61.19}{62.02}$	$\frac{3.28}{3.55}$
Ca.DNTR	296.2902	$\frac{0.92}{190}$	Greenish 219,522	$\frac{8.00}{14.25}$	$\frac{14.00}{14.27}$	$\frac{67.38}{67.50}$	$\frac{3.21}{3.60}$
Sr.DNTR	344.0322	$\frac{0.93}{192}$	Silver Greenish 223,545	$\frac{6.04}{21.06}$	$\frac{21.06}{26.72}$	$\frac{61.85}{62.22}$	$\frac{3.21}{3.54}$

## 2.3. Infrared Spectra study

The important infrared absorption bands and spectra of ligand and its metal complexes are shown in table : 2 and Fig.1 to 4. The spectra of metal complexes are obtained in the range of  $4000 - 400 \text{ cm}^{-1}$  using complex in the form of KBr pellets. The IR spectra indicate the presence of functional groups and metal-oxygen bands in the complex. The drastic reduction in O-H stretching intensity indicates loss of  $2\text{H}^+$  from dantron molecule as a result of coordination. This loss of  $2\text{H}^+$  to give a dianion of dantron is confirmed also by molar conductance values, all complexes being nonconducting in nature. The reduced O-H stretching intensity indicates presence of  $\text{H}_2\text{O}$  molecules of coordination.

**Table 2: Important Infrared spectrum of 1,8-dihydroxyanthraquinone and its chelates**

Functional Group	literature value $\text{cm}^{-1}$	DNTR $\text{cm}^{-1}$	Mg.DNTR	Ca.DNTR $\text{cm}^{-1}$	Sr.DNTR $\text{cm}^{-1}$
O – H S H – Bonded	3500 -3200	3525	3550	3554	3546
-OH S	3300	3370	3413	3412	3411
C-H S	2800	2820	2740	2720	2720
C = O S	1700	1670	1675	1757	1676
C = C S	1610	1620	1624	1625	1626
C – C B	1450	1460	1444	1443	1443
C – H B	1400	1370	1380	1380	1381
C – O S	1200	1200	1203	1210	1211
M – O S	---	---	426,442	417,432	417,405

- Literature values from “reference-9”(S = Stretching , B = Bending)

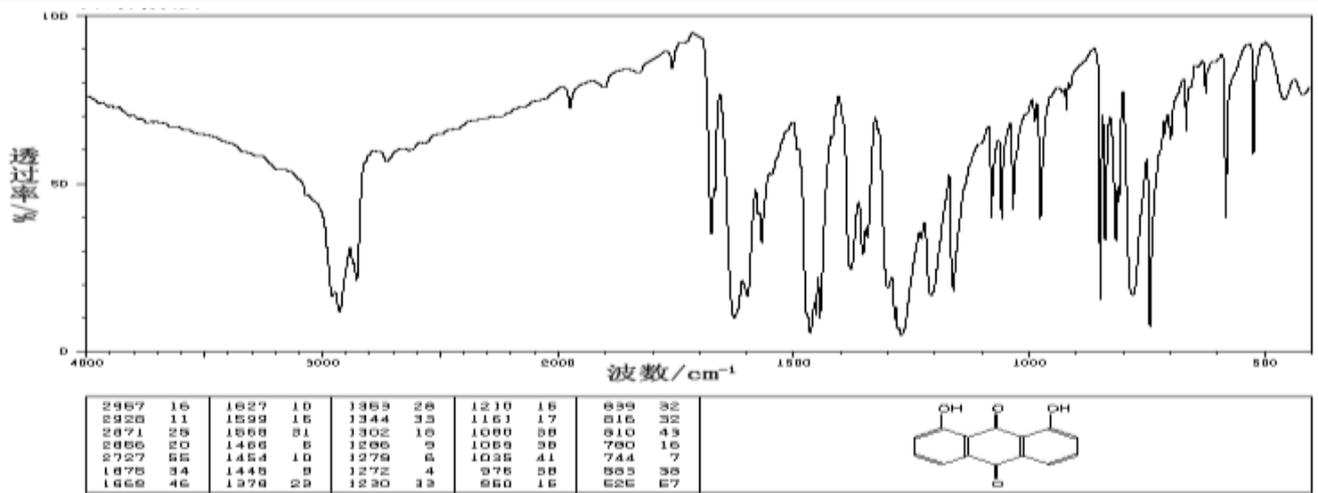


Fig. 1: Infrared spectra of Ligand 1,8-dihydroxyanthraquinone

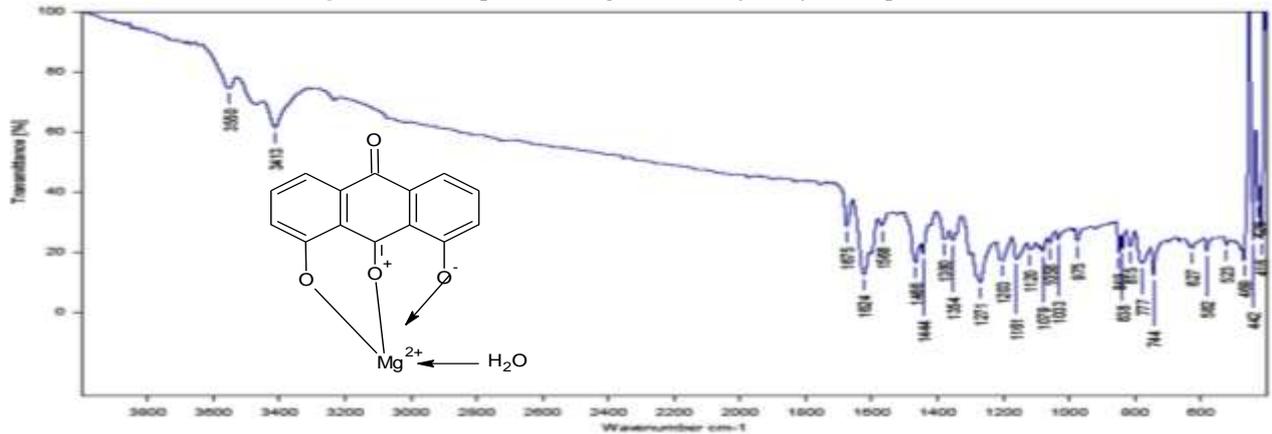


Fig. 2: Infrared spectra of chelate of Mg(II) with Ligand 1,8-dihydroxyanthraquinone

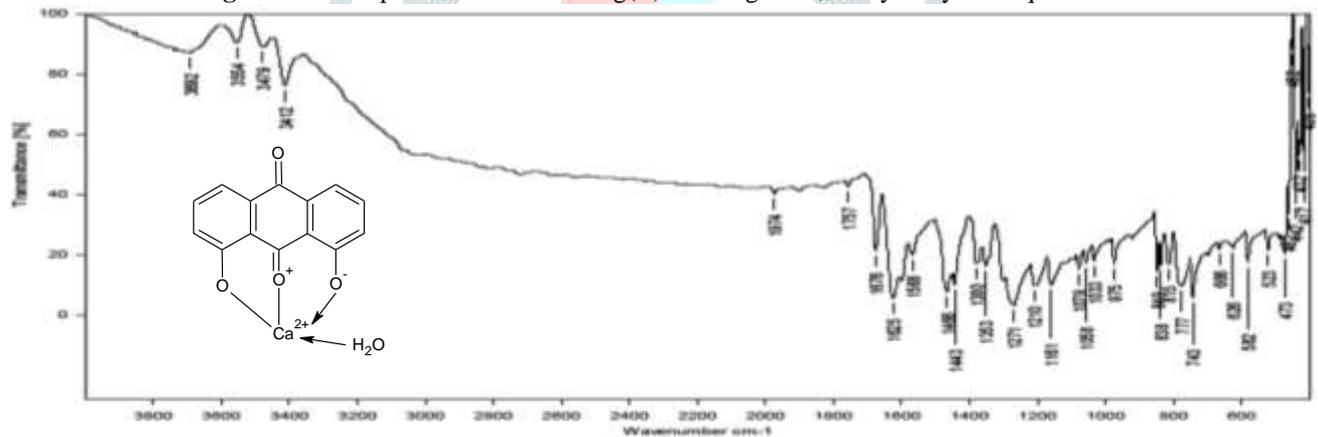


Fig. 3: Infrared spectra of chelate of Ca(II) with Ligand 1,8-dihydroxyanthraquinone

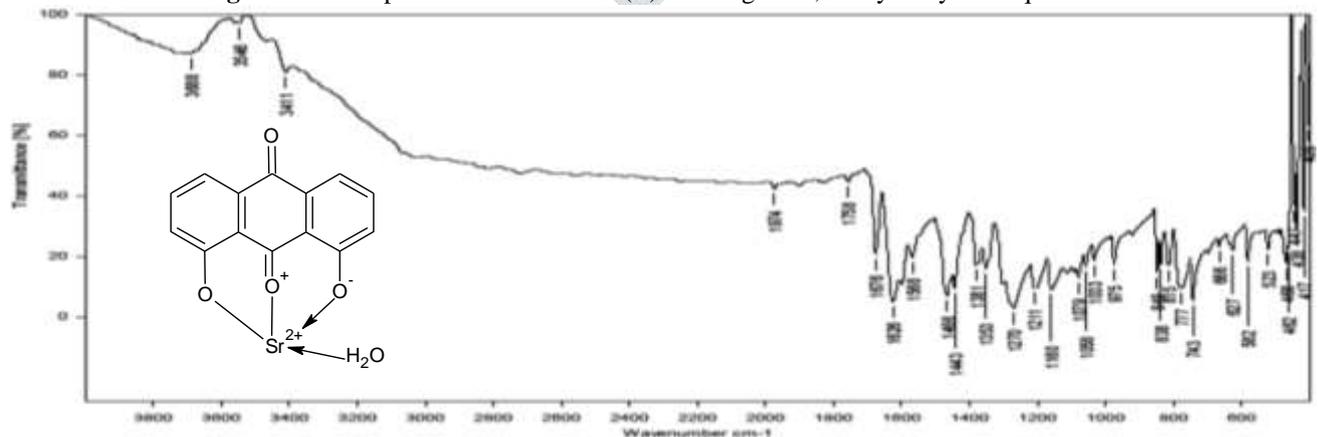


Fig. 4: Infrared spectra of chelate of Sr(II) with Ligand 1,8-dihydroxyanthraquinone

#### 2.4. Electronic Spectral study

The UV- visible absorption spectral data of the maximum absorption wavelength  $\lambda_{max}$  for the ligand and its complexes are shown in table 1. The concentration of the samples prepared was  $(1.0 \times 10^{-6} \text{ M})$  by using DMF as a solvent and the spectrum was recorded at room temperature. The alkaline earth metals magnesium(II), calcium (II) and strontium (II) are typically engaged in chemical bonding as classical main-group elements through their *ns* and *np* valence orbitals, where *n* is the principal quantum number. Analysis

of the electronic structure of these complexes reveals that the metal–C=O bonds arise mainly from  $[M(d_{\pi}) \rightarrow C=O \pi$  back-donation, which explains the strong observed red shift of the C–O stretching frequencies[15].

## 2.5. Thermal Analysis

Thermal analysis includes a group of techniques in which physical property of a substance is measured as a function of temperature program. Thermo gravimetric analysis was carried out for chelates within the temperature range from ambient temperature to 1000°C. The correlation between the different decomposition steps of complexes with corresponding weight losses are discussed in terms of proposed formula of the Ln (III) complexes[16]. The number of water molecules present in the outer sphere and the number of water molecules present in the coordination sphere was determined by thermo gravimetric analysis (TGA). The thermal behavior studies of Mg(II), Ca(II) and Sr(II) complexes are almost same. The No. of molecules of lattice water and Coordination sphere are shown in table 3 (Fig. 5).

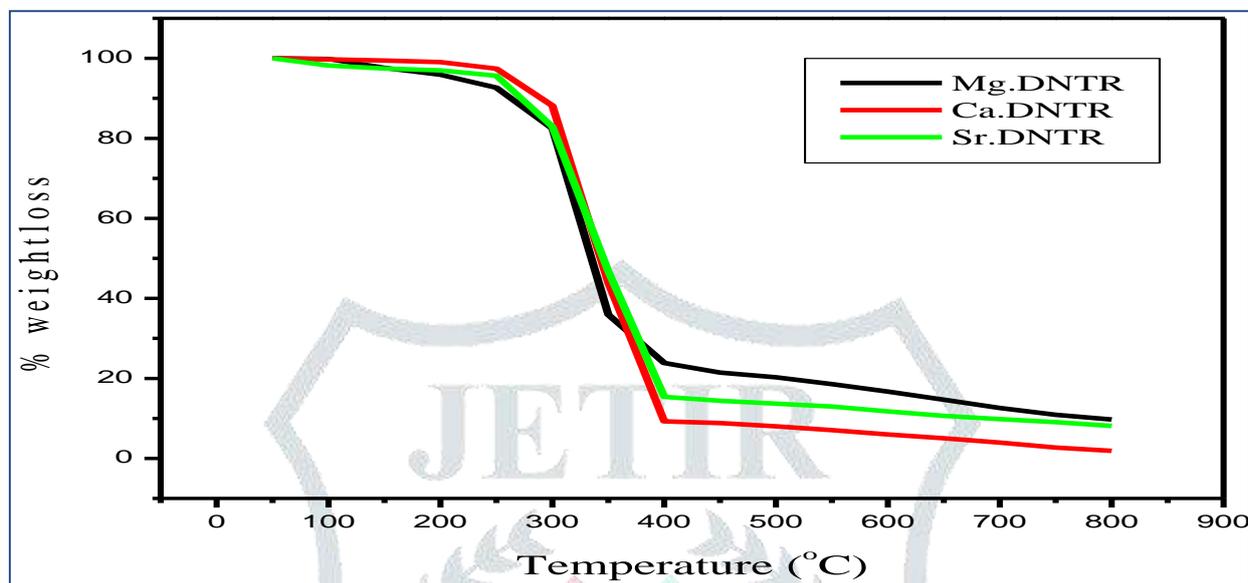


Fig. 5: TGA spectra of chelate of Mg(II), Ca(II) and Sr(II) with Ligand 1,8-dihydroxyanthraquinone

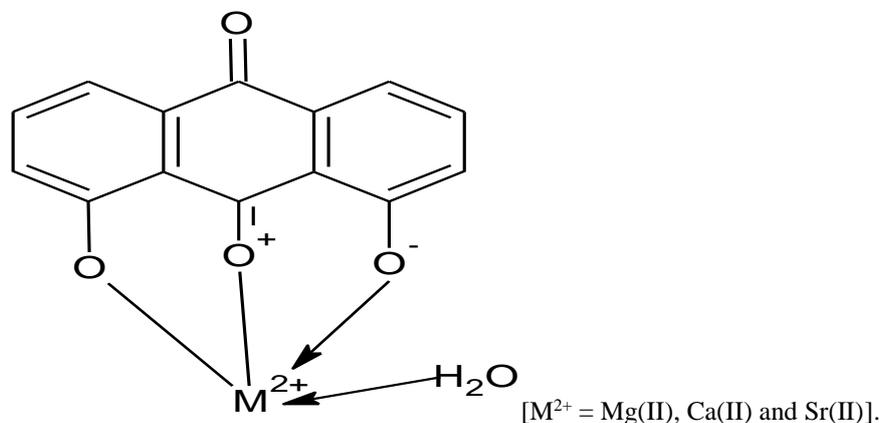
Table 3: Water content and cumulative weight loss data of the metal complexes at 50-250°C

COMPOUND	no. of water molecule found								
	50°C			150°C			250°C		
	%	gms	no. of water molecule	%	gms	no. of water molecule	%	gms	no. of water molecule
Mg.DNTR	0.0	0.0	0	2.38	6.67	0	7.32	20.53	1
Ca.DNTR	0.0	0.0	0	0.54	1.59	0	5.58	16.53	1
Sr.DNTR	0.0	0.0	0	2.54	8.73	0	4.35	14.96	1

## III. RESULT AND DISCUSSION

$\lambda_{\max}$ , Rf, melting point etc suggest complex formation. Molar conductance indicate that complexes are non ionic. IR spectra confirms presence of metal-oxygen bonds and confirmation of coordination too. Using thermal analysis data, one water molecule seems to be present in the coordination sphere. In order to match with tetra coordination, it appears that the fourth coordination site of the metal may be satisfied by the free C–O- part of nearby ligand molecule. This is, in a way, supported by marginal change in –OH stretching frequency as well as drastic reduction in its intensity in the complex in comparison with that of the ligand. CHN analyses also support complex formation process.

**Structures:** From the physicochemical data analysis, the most probable structures of the complexes can be represented as below.



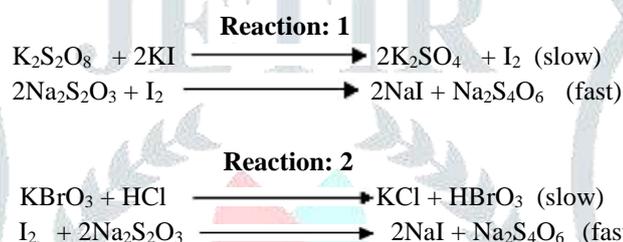
**Fig. 6:** Probable structure of metal chelate with 1,8-dihydroxyanthraquinone ligand

#### IV . APPLICATIONS

In the present work, three different applications of 1,8-dihydroxyanthraquinone complexes have been studied. [a] chemical kinetics [b] catalysis [c] antimicrobial studies

##### 4.1. Chemical kinetics

To find out the catalytic activities of the synthesized complexes, reaction between hydrogen peroxide and hydrogen iodide, potassium bromate with potassium iodide and potassium persulphate with potassium iodide has been carried out. In the entire reaction first step is the rate determining step and all the reactions are of second order reactions [17].

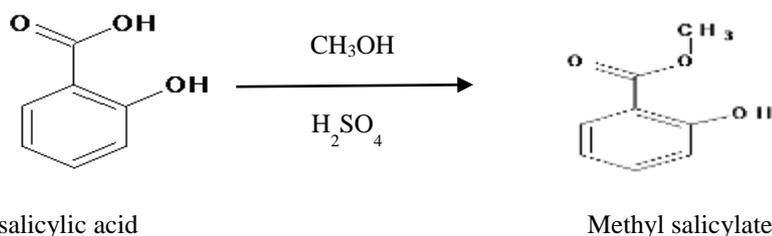


All these second order reactions were performed with and without catalysts. (1 mol %) amount of synthesized metal chelates were used as a catalyst.

**Table 4:** Rate of reactions with and without complexes of 1,8-dihydroxyanthraquinone

Reaction	k without complex	k with Mg. DNTR	k with Ca. DNTR	k with Sr. DNTR	% Increase In reaction Mg. DNTR	% Increase In reaction Ca. DNTR	% Increase In reaction Sr. DNTR
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + KI	3.4922x10 <sup>-5</sup>	3.6772x10 <sup>-5</sup>	4.1591x10 <sup>-5</sup>	3.8844x10 <sup>-5</sup>	5.29	19.09	11.23
KBrO <sub>3</sub> + KI	1.4372x10 <sup>-3</sup>	1.5722x10 <sup>-3</sup>	1.6509x10 <sup>-3</sup>	1.6723x10 <sup>-3</sup>	9.39	14.86	16.35

##### 4.2. Catalysis of organic synthesis reaction



##### Procedure:

A solution of salicylic acid, methyl alcohol and conc. H<sub>2</sub>SO<sub>4</sub> were refluxed for 4 hour in water bath under anhydrous conditions. Excess methanol was removed by distillation and the residual product poured into water. It was extracted with ether, the ether extract washed with sodium bicarbonate solution and finally with water. It was dried and distilled. Methyl salicylate was obtained as a colourless liquid with a fragrant smell. The Boiling point was 223-225 °C.

Table 5: Percentage yield without and with catalyst metal complexes

	Product weight without complex For 3 hours reaction	Product weight with Mg.DNTR For 3 hours reaction	Product weight with Ca.DNTR For 3 hours reaction	Product weight with Sr.DNTR For 3 hours reaction
weight in gram	3.9	4.2	4.4	4.3
% yield	78%	84%	86%	84%
Increase in %	---	7.69 %	10.25 %	7.69 %

### 4.3. Result and discussion

Complexes of dantron with alkaline earth metal ions are capable of increasing the rates of redox reactions, both resulting in liberation of iodine to an extent 5% to 19%. Ca.DNTR complex increased the reaction rate highest among all selected complexes (19%) for persulphate-iodide reaction whereas, Sr.DNTR complex increased the reaction rate of bromate-iodide highest (16%). Remaining all complexes were successful in increasing the rates of the redox reaction. This fact helps to predict that the complexes of alkaline earth metals with dantron seem to be good catalysts which can increase the rates of a number of redox reactions and this would be a very important conclusion useful for industrial applications.

## V. ANTIMICROBIAL ACTIVITY

### 5.1. Experimental

The broth dilution method is used to evaluate the antibacterial activity in the present study. It is one of the non automated in vitro bacterial susceptibility tests. This classic method yields a quantitative result for the amount of antimicrobial agents that is needed to inhibit growth of specific microorganisms. It is carried out in tubes. The main advantage of the 'Broth Dilution Method' for MIC determination lies in the fact that it can readily be converted to determine the MIC as well. Serial dilutions were prepared in primary and secondary screening. The control tube containing no antibiotic is immediately sub cultured [before inoculation] by spreading a loopful evenly over a quarter of plate of medium suitable for the growth of the test organism and put for incubation at 37 °C overnight. The tubes are then incubated overnight. The MIC of the control organism is read to check the accuracy of the drug concentrations. The lowest concentration inhibiting growth of the organism is recorded as the MIC. The amount of growth from the control tube before incubation which represents the original inoculum] is compared. Each synthesized drug was diluted obtaining 2000 microgram /ml concentration, as a stock solution. In primary screening 1000 micro/ml, 500 micro/ml, and 250 micro/ml concentrations of the synthesized drugs were taken. The active synthesized drugs found in this primary screening were further tested in a second set of dilution against all microorganisms. The drugs found active in primary screening were similarly diluted to obtain 200 micro/ml 100 micro/ml, 50 micro/ml, 25 micro/ml, 12.5 micro/ml, 6.250 micro/ml, and concentrations. The highest dilution showing at least 99 % inhibition zone is taken as MIC. The result of this is much affected by the size of the inoculum. The test mixture should contain  $10^8$  organism / ml. The bacterial species used for antibacterial screening were *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa* (*P. aeruginosa*), *Staphylococcus aureus* (*S. aureus*), and *Staphylococcus pyogenus* (*S. pyogenus*). The bacterial species used for antifungal screening were *Candida albicans* (*C. albicans*), *Aspergillus niger* (*A. niger*), *Aspergillus clavatus* (*A. clavatus*). The bacterial species used in this study were obtained from Institute of Microbial Technology, Chandigarh. The results of the compounds synthesized for antibacterial screening and antifungal screening are mentioned in following table no. 6 and table no.7.

Table 6: Comparison of Antibacterial activities (MIC) of the ligand and complexes with standard drugs

Antibacterial Activity of complexes					
Minimum Inhibition Concentration					
Sr	Sample/ standard drug	E.Coli	P.Aeruginosa	S.Aureus	S.Pyogenus
No.	Name	MTCC 443 µg/ml	MTCC 1688 µg /ml	MTCC 96 µg /ml	MTCC 442 µg /ml
1	Ligand DNTR	12.5	12.5	50	25
2	Mg. DNTR	250	250	100	250
3	Ca. DNTR	62.5	100	500	250
4	Sr. DNTR	200	250	250	200
5	Gentamycin	0.05	1	0.25	0.5
6	Ampicillin	100	-----	250	100
7	Chloramphenicol	50	50	50	50
8	Ciprofloxacin	25	25	50	50
9	Norfloxacin	10	10	10	10

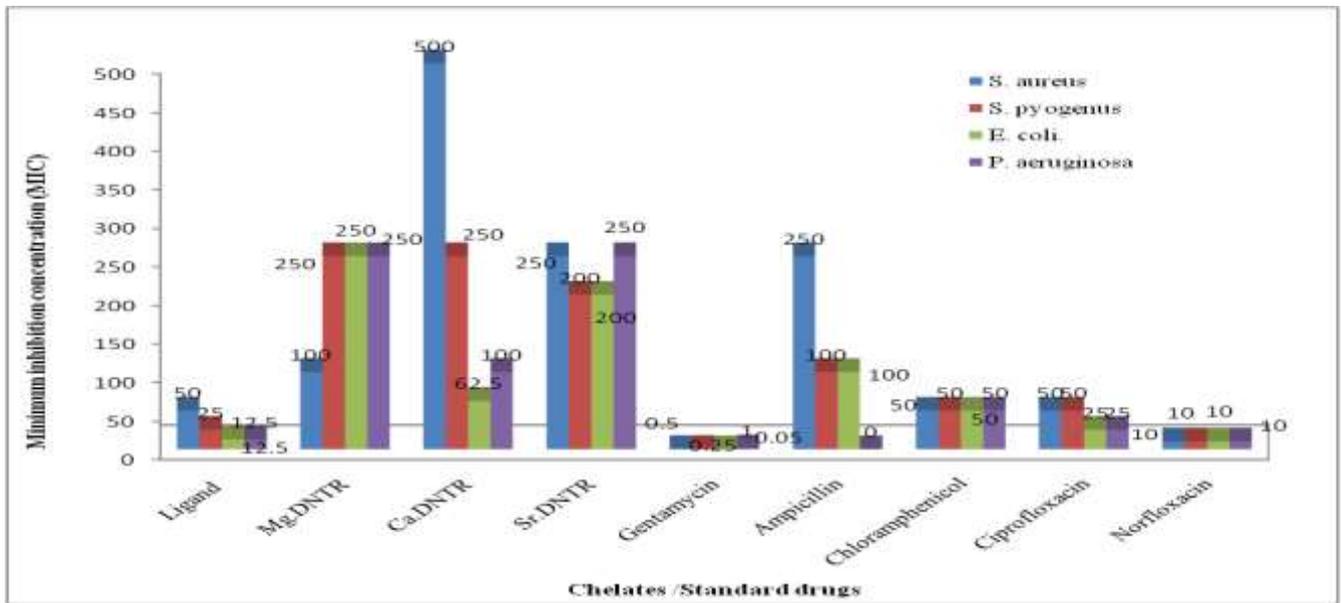


Fig. 7: Comparison of antibacterial activities of metal chelates and standard drugs

Table 7: Comparison of Antifungal activities (MIC) of the ligand and complexes with standard drugs

Antifungal Activity of complexes				
Minimum Inhibition Concentration				
Sr	Sample	C.albicans	A.niger	A.clavatus
No	Name	MTCC 227 µg /ml	MTCC 282 µg /ml	MTCC 1323 µg /ml
1	Ligand DNTR	100	250	250
2	Mg.DNTR	500	500	500
3	Ca.DNTR	250	1000	1000
4	Sr. DNTR	250	>1000	>1000
5	Nystatin	100	100	100
6	Greseofulvin	500	100	100

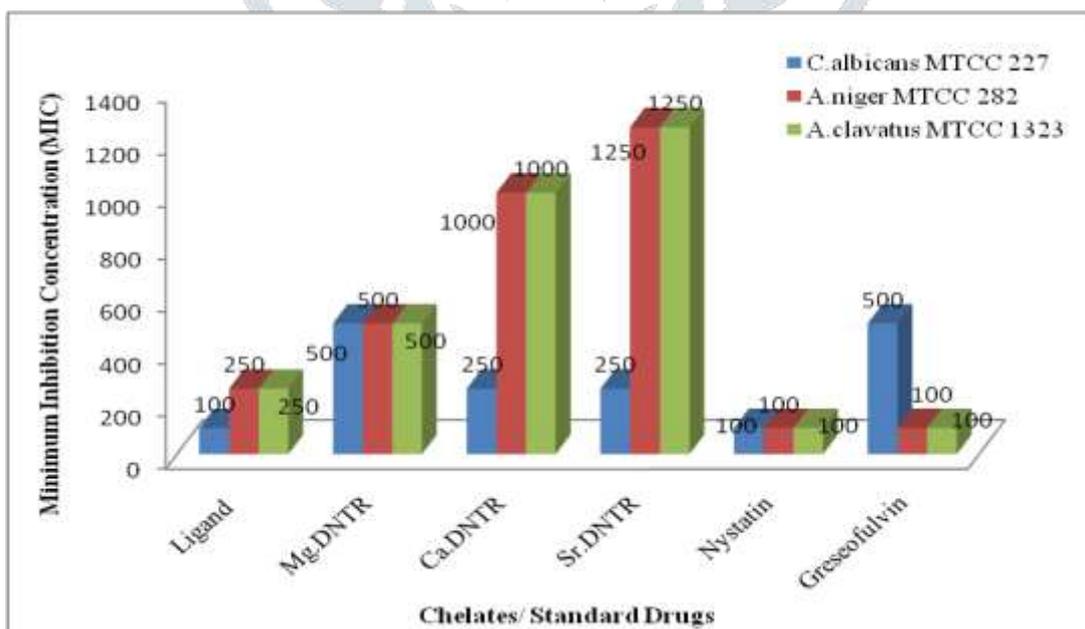


Fig. 8: Comparison of antifungal activities of metal chelates and standard drugs

5.2. Result and Discussion

When subjected to antibacterial activities, it was observed that Ca.DNTR exhibited more activity compared to *ampicillin* against *E.coli*, Mg.DNTR showed more activity compared to *ampicillin* against *S.aureus*. Sr.DNTR showed equal activity as *ampicillin*

against *S.aureus*. Remaining all showed less antibacterial activity against other organisms. In the antifungal activities, Ca.DNTR and Sr.DNTR both showed better activity compared to Greseofulvin against *C.albicans*. Remaining complexes were less active as antifungal compared to standard antifungal antibiotic. Overall, Ca.DNTR exerted better antibacterial and antifungal properties compared to standard antibiotics.

## VI. CONCLUSION

Complexes of dantron with alkaline earth metal ions are capable of increasing the reaction rates of redox and esterification to 19% and 10% respectively. Results of both these homogeneous catalytic experiments are promising and indicate possibility of future industrial application. For many other reactions too. Many of the chelates exerted better antibacterial and antifungal activities compared to standard antibiotics and it would be interesting to explore it further. It quite possible that in conditions where dantron may not be effective but its complexes may be highly effective as antibacterial and antifungal agents.

## CONFLICT OF INTEREST

The author has declared that there is no conflict of interest.

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