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SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL STUDIES OF MANGANESE(II), COBALT(II) AND CADMIUM(II) COMPLEXES CONTAINING OXINE AND 2 – PICOLINE

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ABSTRACT

The complexes of transition metal ions Mn(II), Co(II) and Cd(II) with oxine (8-hydroxy quinoline) and mixed ligand complexes with oxine and 2-picoline have been synthesized. The structural, spectroscopic and thermal properties have been studied on the basis of Infrared spectra, TGA-DTA analysis, X-ray diffraction analysis and Molar conductivity measurements. From the results obtained the following general formula has been given for the complexes $[M(oxine)_2]$ and $[M(oxine)_2(2\text{-}pic)_2]$. The oxine complexes exhibit antiseptic, disinfectant and pesticide properties. So the metal complexes have been tested against microorganisms using Agar well diffusion method in order to assess their antimicrobial properties. The metal complexes were screened for antibacterial activity against gram negative (*Escherichia coli)* and gram positive bacteria *(Bacillus subtilis)* and the fungal activity against *Aspergillus niger* and *Penicillium chrysogenum.*

KEYWORDS: Transition metal complexes, oxine, 2-picoline, Thermal Analysis, Antimicrobial studies.

INTRODUCTION

Transition metals have varying utility and interesting chemistry. Coordination compounds are important due to their role in biological and chemical systems in various ways. It has been observed that metal complexes with appropriate ligands are chemically more significant and specific than the metal ions in original. The mixed ligand complexes are biologically active

against pathogenic microorganisms. Oxine is a monoprotic bidentate chelating agent. Oxine and its metalloquinolates have attracted great interest because of their higher thermal stability. Oxine is the only one, among seven isomeric monohydroxyl quinolines, capable of forming complexes with divalent metal ions through chelation.[1] Most bioactivities of oxine and its derivatives originate from their chelating ability.[2] 2-Picoline was the first pyridine compound reported to be isolated in pure form. The complexation of metallic elements with biologically inactive compounds renders them active and in case the compound is already active, it makes them more active. In this paper, we have investigated the preparation, properties and antimicrobial studies of some metal ions with oxine and 2-picoline.

MATERIALS AND METHODS

Reagents and solvents: All the chemicals ($MnSO_4$, $CoCO_3$ and $CdSO_4$) and reagents used for the preparation of complexes were commercial products (E Merck Ltd, India) and used without further purification. DMF and DMSO were purchased from SRL chem.

Melting points of the synthesised compounds were measured using a melting point apparatus obtained from Guna Enterprises, Chennai.

The IR spectra of the synthesised compounds were recorded using SHIMADZU spectrophotometer in 4000 – 400 cm^{-1} range, using KBr pellet.

The X – ray diffraction patterns of the samples were tested by an X – ray scattering SHIMADUZ XD – DI diffractometer using in filter Cu Kα radiation source (LAMDA = 0.154 nm), set a scan rate = 10 / min, using a voltage of 40 Kv and a current of 30 Ma.

The complexes were tested in a SDT Q600 V8.0 build 95 instrument at Anna University, Chennai. The temperature range was varied from room temperature to 800 °C with heating rate of 20 °C/min in oxygen atmosphere.

The molar conductivities were measured with the conductivity meter of model DCM 900 using the freshly prepared solution of the complexes (10^{-3} M) in DMSO.

The effect of various metal complexes on the several bacterial strains and fungal strains were assayed by Agar well diffusion method.

Preparation of metal complexes

Complexes of the type [M(oxine)$_2$]

5 ml of DMF was added to an aqueous solution of the metal salt in 25 ml water. 5.8 g of oxine was dissolved in 5 ml of DMF, 10 ml of ethanol and 20 ml of 2 M NaOH. Both the solutions were mixed well and heated in a boiling water bath for about three and a half hour. The precipitate formed was filtered using Whatmann no.1 filter paper in hot condition, washed with ether and dried.

Complexes of the type [M(oxine)$_2$(2-pic)$_2$]

5.8 g of oxine was dissolved in 10 ml ethanol and 20 ml of 2 M NaOH. The mixture was added to an aqueous solution of metal salt and stirred for half an hour using a magnetic stirrer. A dense yellow precipitate was formed. To this solution 2 ml of 2-picoline was added slowly and heated in a boiling water bath for half an hour. The precipitate formed was filtered with Whatmann no.1 filter paper, washed with ether and dried.

RESULTS AND DISCUSSION

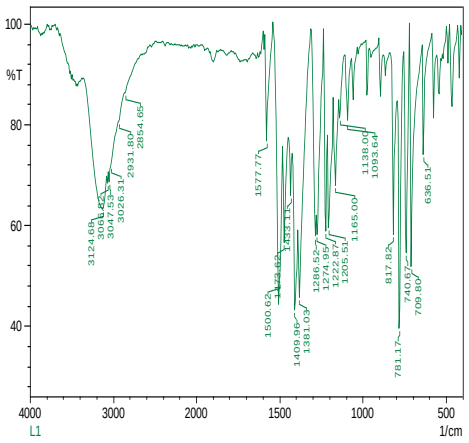
The metal complexes obtained were solid and coloured. They were insoluble in water and soluble in solvents like dimethyl sulphoxide and dimethyl formamide.

Table 1: Analytical data of synthesized transition metal complexes.

Compound	Molecular Formula	Molecular weight	Colour	Melting Point (°C)
[Mn(oxine)$_2$]	$MnC_{18}H_{12}O_2N_2$	343.26	Yellow	>350
[Co(oxine)$_2$]	$CoC_{18}H_{12}O_2N_2$	347.25	Dark Brown	>340
[Cd(oxine)$_2$]	$CdC_{18}H_{12}O_2N_2$	400.72	Bright yellow	>360
[Mn(oxine)$_2$(2-pic)$_2$]	$MnC_{30}H_{26}O_4N_2$	529.52	Yellow	>320
[Co(oxine)$_2$(2-pic)$_2$]	$CoC_{18}H_{12}O_2N_2$	533.51	Brown	>350
[Cd(oxine)$_2$(2-pic)$_2$]	$CdC_{18}H_{12}O_2N_2$	586.98	Bright yellow	>340

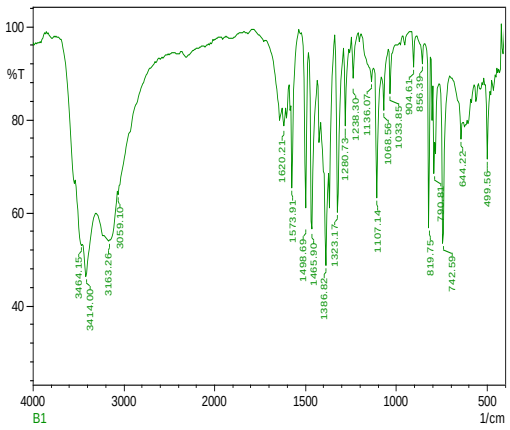
1. Infrared spectra

The IR spectra provide valuable information regarding the nature of the functional groups attached to the metal ion. The transition metal complexes show characterized functional bands such as C-O, C-N, O-H, and C=N groups. Formation of metal-nitrogen and metal-oxygen bonds were further confirmed by the presence of the stretching vibration of υ(M-N) and υ(M-O) around 401-578 cm^{-1} and 648-486 cm^{-1} respectively.



Wavenumber (cm^{-1})

Fig.1: IR Spectrum of oxine

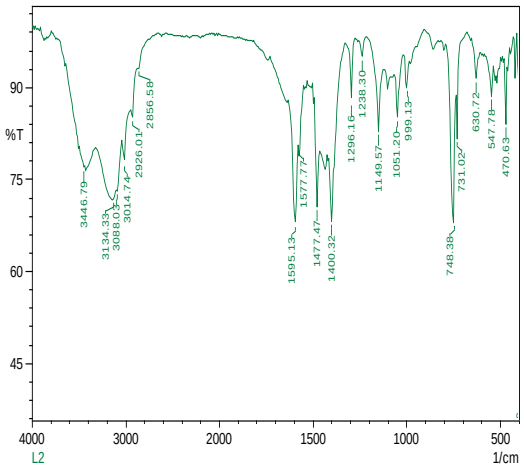


Wavenumber (cm^{-1})

Fig. 2: IR spectrum of [Mn(oxine)$_2$]

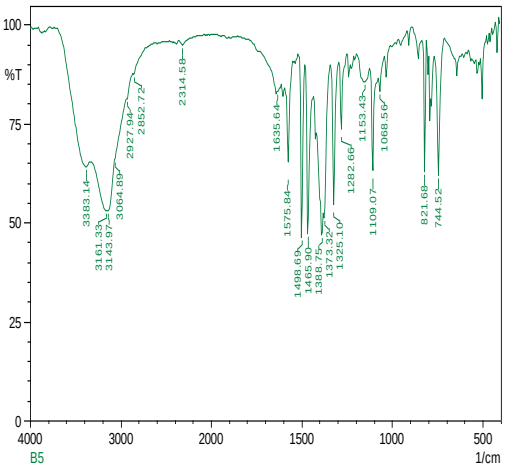
The IR spectrum of the ligand is shown in Fig.1. The spectrum shows the characteristic frequencies of υ(O-H) at 3157.47 cm^{-1}, υ(C-O) at 1278.81 cm^{-1} and υ(C-N) at 1101.35 cm^{-1}. The IR spectrum of [Mn(oxine)$_2$] exhibited a strong band at 1107.14 cm^{-1} and this could be due to υ (C-O) where as other strong bands at 3464.15 cm^{-1}, 1323.17 cm^{-1}, 819.75 cm^{-1}, 742.59 cm^{-1} and 1165.00 cm^{-1} are due to υ(O-H), υ(C-N) respectively. Metal-nitrogen and metal-oxygen bands are further confirmed by the presence of stretching vibration of υ(Mn-N) and υ(Mn-O) are at 499.56 cm^{-1} and 644.22 cm^{-1} respectively.

The IR spectrum of 2-picoline and its complexes



Wavenumber (cm^{-1})

Fig. 3: IR Spectrum of 2-picoline



Wavenumber (cm^{-1})

Fig. 4: IR spectrum of [Co(oxine)$_2$(2-pic)$_2$]

The band appeared at1587.42 cm^{-1} in Fig.3 indicate the presence of C=N linkage. Bands appeared at 2926.01 cm^{-1} and 2856.58 cm^{-1} are due to the presence of –CH_3 group.[3] The IR

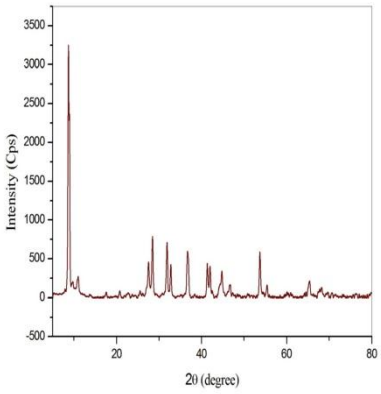
spectrum of the sample is shown in Fig.4. The spectra exhibited strong bands at 1109.7 cm^{-1} and 1282.66 cm^{-1} and this could be due to υ(C-O). Vibrations due to aromatic ring appear at 3064.89 cm^{-1}, 1575.84 cm^{-1} and 1465.90 cm^{-1}. Metal-nitrogen and metal-oxygen bands were further confirmed by the presence of stretching vibration of υ(Co-N) and υ(Co-O) at 503.14 cm^{-1} and 642.30 cm^{-1} respectively.[4]

2. X-Ray Diffraction Analysis

XRD analysis is used to determine the percentage of crystallinity present in the material. The crystal size has been calculated using Debye-Scherrer's equation.[5]

Table 2: X-Ray Diffraction of the Complexes.

Complexes	FWHM (deg)	2θ (deg)	Crystal size (nm)
$[Mn(oxine)_2]$	0.3053	8.654	26.0987
$[Co(oxine)_2]$	0.4594	8.713	17.3449
$[Cd(oxine)_2]$	0.2593	8.529	30.7261
$Mn(oxine)_2(2\text{-pic})_2]$	0.3748	8.653	21.2591
$[Co(oxine)_2(2\text{-pic})_2]$	0.3354	23.471	24.1943
$[Cd(oxine)_2(2\text{-pic})_2]$	0.2959	22.558	27.3796



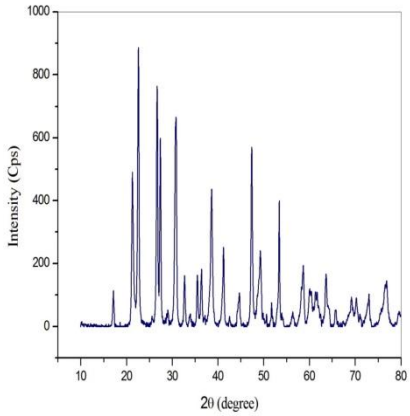
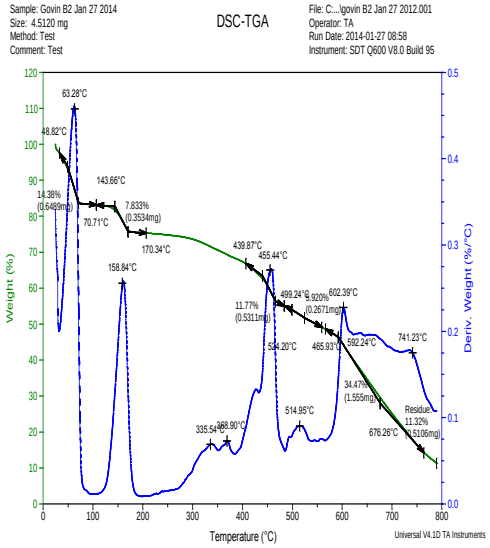


Fig. 5: X-Ray Diffraction of $[Co(oxine)_2]$ Fig. 6: X-Ray Diffraction of $[Cd(oxine)_2(2\text{-pic})_2]$

3. Thermal Data

The thermal properties for metal oxine complexes and metal oxine and 2-picoline complexes have been investigated. All the stages of decomposition follow one after the other without any stable compound in between.[6] The exothermic peaks are due to oxidative degradation of the complexes.



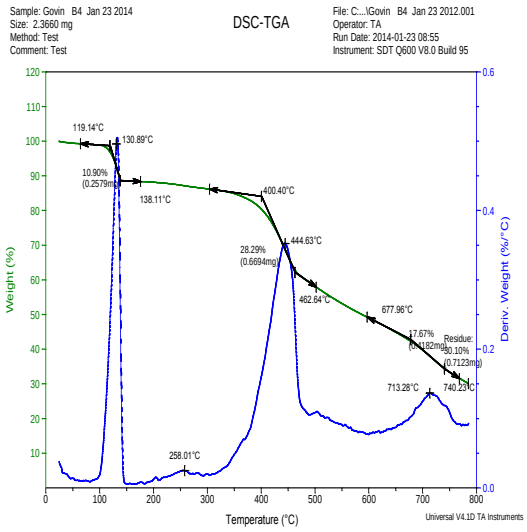


Fig. 5: Thermal data of $[Co(oxine)_2]$ **Fig. 5: Thermal data of $[Mn(oxine)_2(2\text{-pic})_2]$**

4. Molar Conductance

The synthesized transition metal complexes were dissolved in DMSO and the molar conductivities of 10^{-3} M solution at 25±2 °C were measured. The molar conductivity values of the complexes are given in table-3.

Table 3: Molar Conductance data of the complexes.

Compound	Specific Conductance $ohm^{-1} cm^2$	Molar Conductance $ohm^{-1} cm^{-2} mol^{-1}$
$[Mn(oxine)_2]$	0.04×10^{-6}	0.04
$[Co(oxine)_2]$	0.04×10^{-6}	0.04
$[Cd(oxine)_2]$	0.04×10^{-6}	0.04
$[Mn(oxine)_2(2\text{-pic})_2]$	0.04×10^{-6}	0.04
$[Co(oxine)_2(2\text{-pic})_2]$	0.04×10^{-6}	0.04
$[Cd(oxine)_2(2\text{-pic})_2]$	0.04×10^{-6}	0.04

The measured molar conductance of all synthesized transition metal complexes were of 0.04 $ohm^{-1} cm^{-2} mol^{-1}$. The lower molar conductivity values showed the non-electrolytic nature of the complexes.[7]

5. Antimicrobial Studies

Bioeffiency of the transition metal complexes were tested against bacteria such as *Bacillus species*, *E. coli* and fungi like, *Aspergillus niger and Pencillium chrysogenum* using well diffusion method.

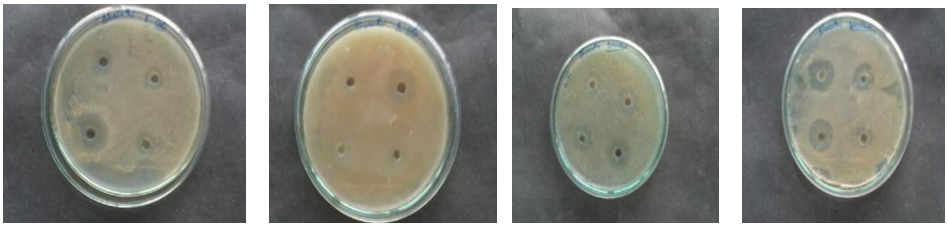
Antibacterial Activity of Metal Complexes

The antibacterial activities of complexes were studied using Agar well diffusion method. The bacterial species used in the screening were *Bacillus species* (gram positive) and *E. coli* (gram negative).

The diameter of zone of inhibition was calculated in millimeters. The well diameter was detected from the zone diameter to get the actual zone of inhibition and the values have been tabulated. The results indicate that most of the test compounds exhibit very good antibacterial and antifungal activity.[8]

IMAGES OF ANTIBACTERIAL ACTIVITY

ESCHERICHIA COLI BACILLUS SPECIES



$[M(oxine)_2]$ $[M(oxine)_2(2\text{-}pic)_2]$ $[M(oxine)_2]$ $[M(oxine)_2(2\text{-}pic)_2]$

Table 4: Antifungal Activity of Metal Complexes.

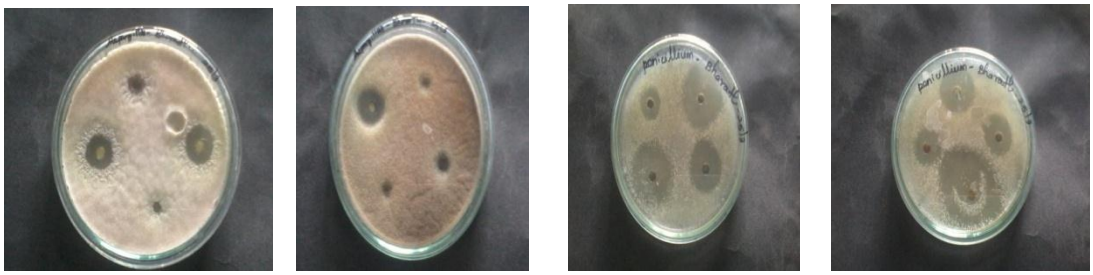
Complexes	Concentration	Zone of inhibition(in diameter)		
		E. coli	*Bacillus species*	*Ampicilln* (standard)
$[Mn(oxine)_2]$	1 mg/ml	13	17	16
$[Co(oxine)_2]$	1 mg/ml	15	14	16
$[Cd(oxine)_2]$	1 mg/ml	13	15	16
$[Mn(oxine)_2(2\text{-}pic)_2]$	1 mg/ml	19	18	16
$[Co(oxine)_2(2\text{-}pic)_2]$	1 mg/ml	10	14	16
$[Cd(oxine)_2(2\text{-}pic)_2]$	1 mg/ml	12	24	16

Antifungal Activity of Metal Complexes

The Antifungal activity of standard fungicide (*polymyxin*) and complexes were tested for their effects on the growth of microbial cultures and studied for their interaction with *Aspergillus niger* and *Penicillium chrysogenum*. The zone of inhibition measured for standard and complexes have been listed below.

IMAGES OF ANTIFUNGAL ACTIVITY

ASPERGILLUS NIGER ***PENICILLIUM CHRYSOGENUM***

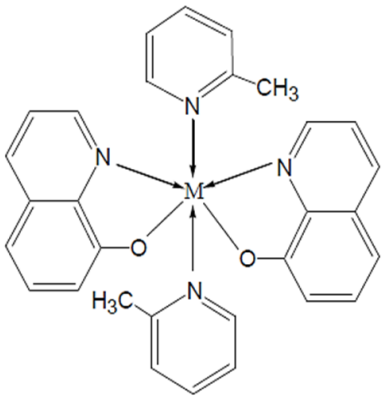


[M(oxine)$_2$] **[M(oxine)$_2$(2-pic)$_2$]** **[M(oxine)$_2$]** **[M(oxine)$_2$(2-pic)$_2$]**

Table 5: Antifungal Activity of the Metal Complexes.

Complexes	Concentration	Zone of inhibition(in diameter)		
		Aspergillusniger	***Penicilliumchrysogenum***	***polymyxin* (standard)**
[Mn(oxine)$_2$]	1 mg/ml	12	31	11
[Co(oxine)$_2$]	1 mg/ml	-	16	11
[Cd(oxine)$_2$]	1 mg/ml	15	24	11
[Mn(oxine)$_2$(2-pic)$_2$]	1 mg/ml	5	27	11
[Co(oxine)$_2$(2-pic)$_2$]	1 mg/ml	5	20	11
[Cd(oxine)$_2$(2-pic)$_2$]	1 mg/ml	16	23	11

The results are corroborated with the findings of other researchers ([3]). The proposed structure of the complexes is given below.



where M = Mn^{2+}, Co^{2+} and Cd^{2+}.

CONCLUSIONS

The complexes of Mn(II), Co(II) and Cd(II) were synthesised using oxine as ligand and also with mixed ligands oxine and 2-picoline. The complexes were coloured and they are insoluble in water and soluble in DMF and DMSO. The Complexes were characterized by melting point, solubility, molar conductance, IR spectra, XRD and TGA-DTA techniques.

The metal oxine complexes and metal oxine, 2-picoline complexes exhibit good activity aganist bacterial strains Gram positive (*Bacillus species)* and Gram negative*(Escherichia coli)*, fungal strains such as (*Aspergillus niger, Penicillium chrysogenum)* compared with the standard drugs. The increase in antimicrobial activity may be due to metal chelation. Manganese and cadmium chelates are highly active due to the combined effect of Mn(II) and Cd(II) and its functional groups present in the ligands.

The lower conductivity values indicated the non-electrolytic nature of the complexes. The melting points of metal chelates are higher which suggests their thermal stability. The thermal degradation steps were identified and are mainly due to the direct decomposition of oxine and 2-picoline from metal complex leaving the corresponding metal oxide. The exothermic peaks are due to oxidative degradation of the complexes. The XRD of the complexes were studied. The complexes $[Co(oxine)_2(2\text{-}pic)_2]$ and $[Cd(oxine)_2(2\text{-}pic)_2]$ are found to be crystalline and the other complexes are found to be semicrystalline. The structure assignment cannot be considered final in the absence of X-ray crystal studies.

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