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Synthesis, spectral and biological studies of Cr(III), Mn(II) and Fe(II) complexes with diacetylmonoxime

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ABSTRACT

A bidentate Schiff base ligand namely diacetylmonoxime2/3-nitroaniline were synthesized by condensing o/m-nitroaniline with diacetylmonoxime. Cr (IIII), Mn (II) and Fe (II) complexes of the chelating ligands were synthesized using chlorides of these metals. The ligands and the complexes were characterised by elemental analysis, spectral (I.R., U.V.-Visible, Mass) analysis, x-ray powder diffraction, magnetic susceptibility measurements. An octahedral structure is proposed for Cr (IIII), Mn (II) and Fe (II) complexes on the basis of magnetic and spectral measurements. Spectroscopic studies indicate that the coordination occurs through oxime oxygen after deprotonation and nitrogen of azomethine. A triclinic system was proposed by x-ray diffraction study of metal complexs. Anti-bacterial and anti-fungal activity of the schiff base ligands and their metal complexes have been studied using the agar well diffusion method and ditch diffusion method. Ligands and metal complexes shows activity against S. aureus (gram positive), P. aeruginosa (gram negative) Aspergillus niger and Candida albicans.

Key words: Schiff bases, transition metal complexe, Antifungal and antibacterial activity, X-ray powder diffraction study, Triclinic crystal system.

INTRODUCTION

Metal complexes of heterocyclic acids and their derivaties had attracted by many workers[1-3] due to their biological, pharmacological, clinical and analytical importance. Thiophene derivatives are well known to exhibit an array of biological activity such as antibacterial and antifungal activity[4,5,6]. Condensed thienopyrimidines exhibit interesting antibacterial activity[7,8]. There is enormous interest presently in the field of coordination chemistry of later '3d' transition metals with Schiff bases. They have also been used as biological models[10], oxygen carriers and drugs[11]. Some Studies of metal complexes of diacetylmonoxime and their related ligands have been reported[12, 13].

In this paper, it has been reported the preparation and characterizations of metal complexes derived from diacetylmonoxime 2/3-nitroaniline (2-NAD, 3-NAD) with transition metals ions like Cr (III), Mn (II) and Fe (II). The main interest in this ligand originates in its oxime group containing -N-O- donar atom.

EXPERIMENTAL

2-NAD was prepared according to the literature method[13, 14]. All the chemicals used for synthesis were analytical grade. Diacetylmonooxime was obtained from Thomas Baker and Nitroaniline was obtained from Aldrich.

Synthesis of diacetylmonoxime2-nitroaniline (Ligand)

Diacetylmonoxime (1.0gm) and o/m-nitroaniline (1.5gm) were dissolved separately in absolute alcohol and mixed together and refluxed for 4 hrs. on water bath. After heating insoluble materials were removed by filtration and cooled. A yellow brown needle shaped 2/3-NAD was formed, washed it with absolute alcohol and then dried over

anhydrous $CaCl_2$. Yield of both ligands were 100%. The melting point of the 2NAD = 355K and 3NAD= 368K. The molecular formula of ligands $C_{10}H_{11}N_3O_3$ {for 2NAD found C = 54.30%, H = 4.97%, N = 19.0%; calculated C = 54.32%, H = 4.90%, N = 18.9% and for 3NAD= found C=54.15%, H=4.85%, N=19.05%; calculated C=54.32%, H=4.90, N=18.90 %.}

Synthesis of Metal Complexes

The prepared ligand and metal salts in 1:1 proportion were dissolved separately in absolute alcohol and mixed together and refluxed for 4 hrs. On water bath. After cooling insoluble materials are removed by filtration, coloured crystalline metal complexes were formed , recrystalised and dried over anhydrous $CaCl_2$.

Antibacterial activity and Antifungal activity

The synthesized ligands and complexes were screened for in vitro growth inhibitory activity against Gram positive bacteria *Staphylococcus aureus* and Gram negative bacteria *Pseudomonas aeruginosa*. Nutrient agar plates were made uniformly surface inoculated from the culture of the tested microorganisms. Well was made on the agar medium at the centre. Normal saline was used to prepare the inoculum of the bacteria to be used for the antibacterial study[9].

The synthesized ligands and complexes also screened for in vitro growth inhibitory activity against *Aspergillus niger* and *Candida albicans. Sabouraud dextrose* agar plates made uniformly. Ditch made on the agar medium at the centre. Two separate striking lines of fungi were made on both the sides of ditch[6,9].

Mueller Hint Agar Media (HI Media) was used to subculture various strains of microorganisms.

The lowest concentration of the compound which shows positive antibacterial and antifungal activity was subjected to dilution method for quantitative measurement of micro static (inhibitory) activity.

The lowest concentration which completely inhibited visible microbial growth was recorded as the Minimum inhibitory concentration (MIC, µg/ml)[5,8]. The stock solution of the test compounds (0.04mg/ml) was prepared in DMF and subsequent dilutions(80%, 60%, 40%, 20%) of stock solutions were made in the same solvent. Under strict aseptic conditions, the diluted test solutions with different concentrations were added to the disc and ditch separately with numbered plates. Then the plates were incubated at 310K for 24 hr. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. Antibacterial activity was indicated by the presence of clear inhibition of zone around the well and antifungal activity was indicated by the presence of inhibition of zone nearer to the ditch.

RESULTS AND DISCUSSION

The complexes are stable in air but decomposed at high temperature. Easily soluble in Dimethylformamide (DMF) and dimethylsulphoxide (DMSO).

Electronic Spectra and Magnetic moment

The solid state electronic spectra of the complexes were recorded. In table1, lists the important electronic spectral bands of the complexes.

The electronic spectrum of ligands and complexes helps to indicate the geometry. The electronic spectra of the ligand shows strong absorption bands in the region 175 to 250nm but in complexes they are slightly shifted to higher frequency[17]. These are $\pi \rightarrow \pi^*$ charge transfer transitions.

The bands in the region 360 to 410nm can be assigned to the $n \rightarrow \pi^*$ transitions of the azomethine group. In the spectra of the complexes the bands of the azomethine chromophore $n \rightarrow \pi^*$ transitions are shifted to lower frequencies indicating that the imine nitrogen atom is involved in coordination to the metal ion[18]. Those very low intensity absorption bands associated with d-d transitions for Cr complexes are 590-595nm, 502-508nm, for Mn complexes are 615-620nm, 580-590nm and for Fe complex 482-492nm Supports the coordinated geometry of the metal complexes[18,19].

The room temperature magnetic moment values also help to indicate the geometry. The magnetic moment value of Cr (III)complex is in the rang 3.7 to 3.9BM, is close to theoretical spin only value (μ_{eff} = 3.98BM) for Cr^{3+} (d^3 system), Mn (II) in the rang 5.6 to 6.0BM is close to theoretical spin only Value (μ_{eff} = 5.67BM) for Mn^{2+} (d^5 system) and Fe (II) in the rang 4.6 to 5.1BM is close to theoretical spin only value (μ_{eff} = 4.637BM) for Fe^{2+} (d^6 system) indicates octahedral geometry of the complexes[20].

Infrared Spectra

The I.R. bands of ligands and metal complexes are listed in table 4.Thee I.R. spectra of the complexes shows, complexes behave as a bidentate coordinating ligand via the azomethine nitrogen (C=N*) and oxygen of oxime (-NOH) group by replacement of hydrogen ion forming six membered ring around metal ion[13].

In the ligand azomethine (C=N*) group is at high wavenumber but in metal complexes it shifts to lower wavenumber, this indicates that imine nitrogen atom involved in coordination to the metal ion[17, 21] while oxime (C=N) remain more or less at the same position. The N-O band in ligand at 932 cm^{-1} but in metal complexes it shifts to higher wavenumber, this indicates that oxygen atom by replacing oxime proton involved in coordination to the metal ion[13, 19]. A broad band observed in the ligand at about ~3330 due to N-H group present in the imidazole ring which is rarely observed in metal

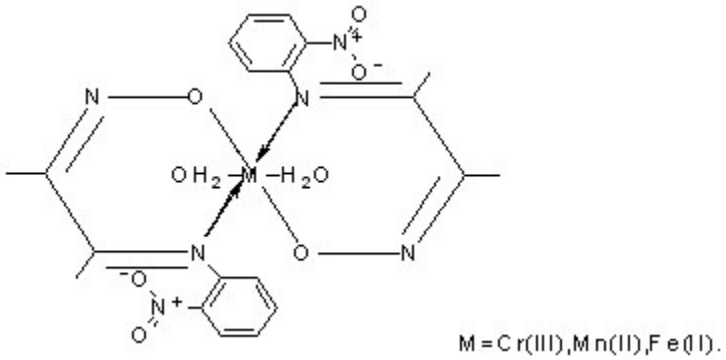

Fig.1: Structural presentation of M-2NAD. $2H_2O$

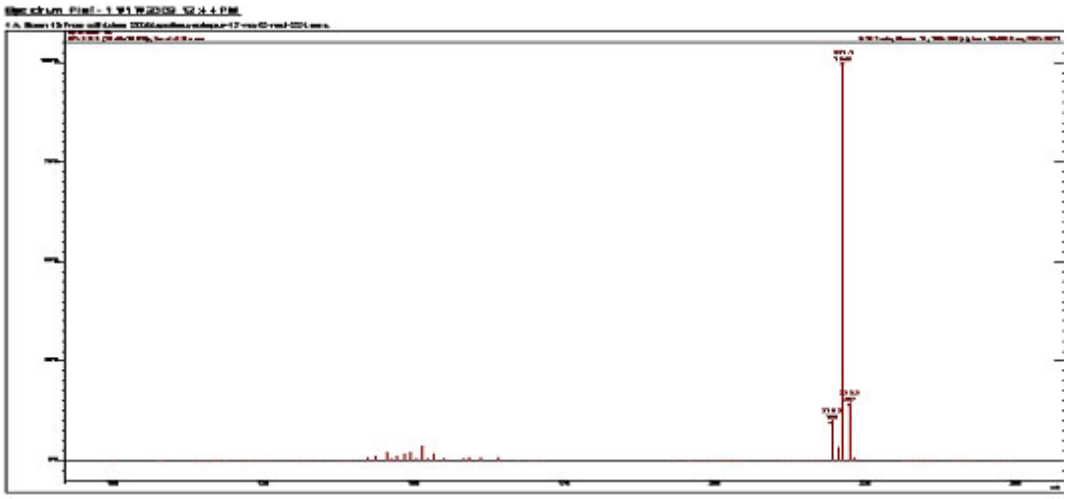

Fig. 2: Mass Analysis of 2NAD

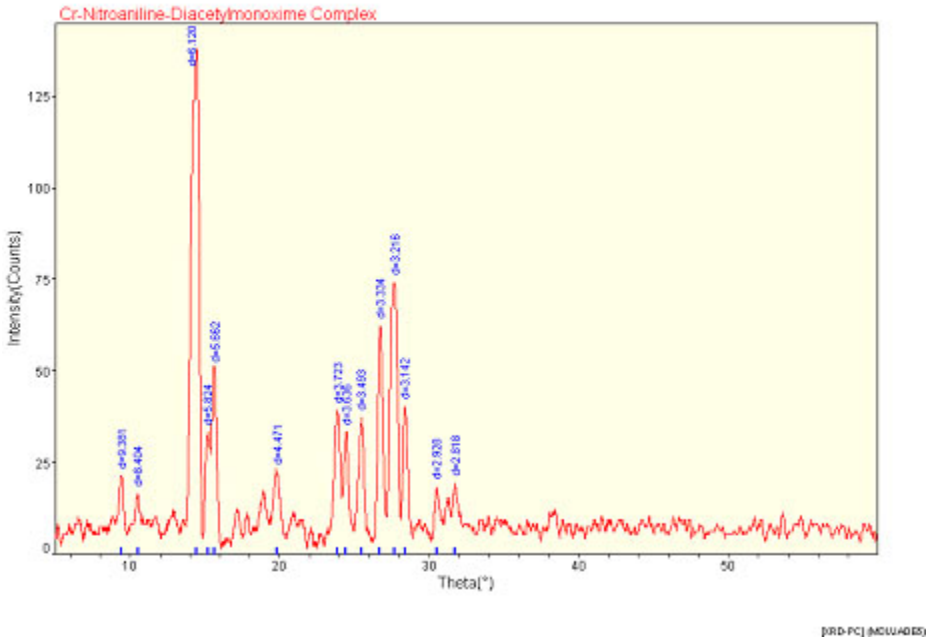

Fig. 3: X-rd powder diffraction-

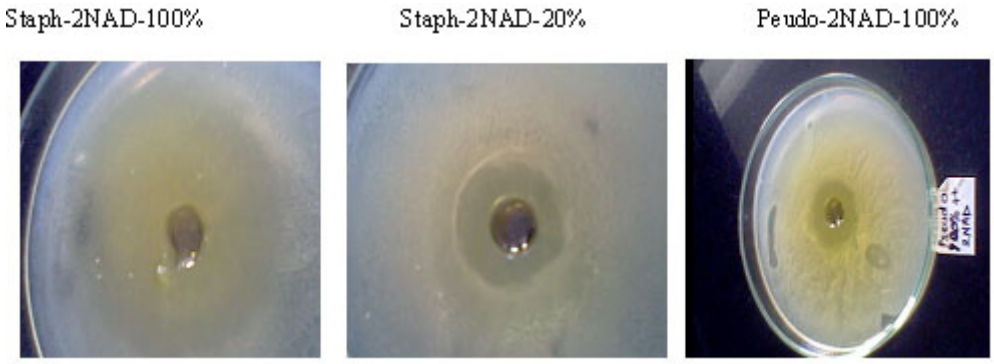

Fig. 4: Antibacterial activity

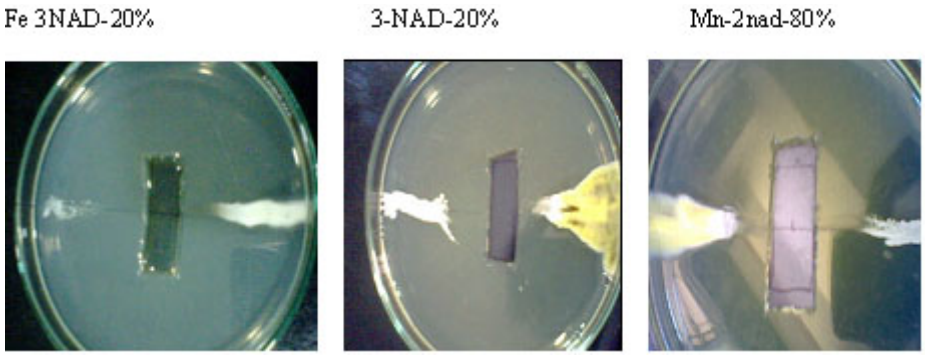

Fig. 5: Antifungal activity

complexes. A broad band observed in all the complexes in the rang ~3470 cm^{-1} due to õoí of the coordinated H_2O. This is supported by the appearance of an additional band in the rang 900-850 cm^{-1} for (O-H) rocking deformation and 750-700 cm^{-1} for (O-H) agging mode of coordination which is not observed in the ligand spectrum[19]. Thus H_2O is coordinated in metal complexes. New bands appear in the 450-420 and 360-305 cm^{-1} assignable to the υ(M-O) and υ(M-N) respectively in metal complexes only[17,23]. Asymmetric stretching of aromatic nitro compound remain at the same position at 1345 cm^{-1} which does not take part in complexation[13, 20]. Thus proposed octahedral geometry of the complexes is in fig.1.

Mass analysis

The formation of ligand proved by the appearance of a peak at 221.21e/z which is a molecular weight of ligand[25] Fig. 2.

X-ray Analysis

Single crystal X-ray crystallographic investigation is the most precise source of information regarding the structure of the complex, the difficulty of obtaining crystalline complexes in proper symmetric form has rendered the powder X-ray diffraction method for such study. The X-ray diffraction pattern of the complexes indicates high crystallinity of the complexes. The diffractogram of Cr-2NAD.$2H_2O$ complex records 14 reflections between 8 to 50(2θ) with maximum at 2θ = 14.46 corresponding to value of d = 6.1205A (refer table 3). The main peaks of the complex have been indexed by using computer software by trial and error method[26,27], keeping in mind characteristics of various symmetry systems till good fit could be obtained between observed and calculated 2θ and $\sin^2\theta$ values. The method also yielded *h k l* (miller indices) values. The relative intensity corresponding to the prominent peaks have been measured.

Table 1: Electronic spectral data and magnetic values of the metal complexes

Name of the compounds	μeff (BM)	π→π*and π→π* transitions and charge transitions(nm)	d-d transitions
2-NAD(yellow brown)	-	225, 410	-
Fe-2NAD(red brown)	4.637	230, 346	588, 492
Cr-2NAD(dark red brown)	3.984	235, 360	590
Mn-2NAD(dark blue brown)	5.670	250, 360	502, 615, 700
3-NAD(yellow brown)	-	225, 410	-
Fe-3NAD(red brown)	4.638	230, 346	587, 494
Cr-3NAD(dark red brown)	3.983	235, 360	595
Mn-3NAD(dark blue brown)	5.672	250, 360	500, 615, 705

Table 2- I.R. bands of ligands and metal complexes.

Name of the compounds	υ(C=N*)	υ(C=N)	υ(N-O)	υ(M-O)	υ(M-N)	υ(C-NO_2)
2-NAD	1632	1569	955	-	-	1345
Fe-2NAD	1625	1560	1100	440	360	1346
Cr-2NAD	1625	1565	1100	450	350	1346
Mn-2NAD	1630	1569	1101	435	309	1349
3-NAD	1630	1567	955	-	-	1345
Fe-2NAD	1624	1560	1100	448	358	1347
Cr-2NAD	1625	1563	1105	440	355	1346
Mn-2NAD	1625	1569	1100	438	315	1345

A comparison of values of 2θ and $\sin^2\theta$ for the complex reveals that, there is good agreement between the calculated and observed values of 2θ and $\sin^2\theta$ on the basis of assumption of triclinic structure[28]. The small difference in the observed d-spacing can be attributed to the difference in unit cell dimensions. The structure of Cr-2NAD.$2H_2O$ complex yields values for lattice constant a = 8.5532A, b = 9.5170A and c = 8.7424A; α = 99.303D, β = 100.394D and γ = 90.903D; the unit cell volume V^3 = 690.02. In conjugation with these lattice parameters the condition such as $a \neq b \neq c$ and of $\alpha \neq \beta \neq \gamma$ required for the sample to be triclinic were tested and found to be satisfactory. Refer fig. 3.

Biological activity

Antibacterial activity - The synthesized ligands and complexes were screened for in vitro growth inhibitory activity against gram positive bacteria *Staphylococcus aureus* and Gram negative bacteria *Pseudomonas aeruginosa*. A comparative study of Schiff bases and metal complexes indicate that the metal complexes exhibit higher antibacterial activity than the free ligands. The inhibitory zones of the ligands and metal complexes are shown in table 4. Fig.4 shows the difference between inhibitory zones of ligand and the metal complex.

Table 3: X-ray Diffraction data of Cr-2NAD.$2H_2O$

d-spacing obs.	d-spacing cal.	I%	Miller Indices h k l	$\sin^2\theta$ obs.	$\sin^2\theta$ cal.	2θDeg. obs.	2θDeg. cal.
9.3818	9.3818	11.8	0 1 0	67.4	67.4	9.42	9.42
8.4038	8.4038	7.1	1 0 0	84.0	84.0	10.52	10.52
6.1205	6.1205	100.0	1 1 0	158.4	158.4	14.46	14.46
5.8241	5.8241	17.3	0 1 1	174.9	174.9	15.20	15.20
5.6616	5.6616	33.9	-1 -1 1	185.1	185.1	15.64	15.64
4.4713	4.4713	11.8	1 1 1	296.8	296.8	19.84	19.84
3.7233	3.7692	26.8	-2 1 1	428.0	435.3	23.88	24.08
3.6362	3.6411	19.7	0 1 2	448.7	447.5	24.46	24.43
3.4929	3.4922	24.4	1 -1 2	486.3	486.5	25.48	25.49
3.3336	3.3264	40.2	-1 -2 2	533.9	536.2	26.72	26.78
3.2156	3.2146	48.0	-2 -1 2	573.8	574.2	27.72	27.73
3.1422	3.1439	21.3	1 1 2	600.9	600.3	28.38	28.36
2.9285	2.9358	8.7	-1 -3 1	691.9	688.4	30.50	30.42
2.8184	2.8202	8.7	-3 0 1	746.9	746.0	31.72	31.70

Table 4: Antibacterial activity

Name of	*Pseudomonas* (cm)					*Staphylococcus Aureus* (cm)				
compound	20%	40%	60%	80%	100%	20%	40%	60%	80%	100%
2NAD	-	-	-	-	+(1.8)	-	-	-	+(1.7)	+(2.0)
Fe-2NAD	-	-	+(1.8)	+(2.0)	++(2.2)	-	-	+(1.9)	+(2.1)	+(2.2)
Cr-2NAD ++(2.3)	-	+(1.9)	+(1.7)	++(2.1)	++(2.3)	-	+(1.8)	+(1.9)	+(2.1)	
Mn-2NAD	-	-	-	+(1.7)	+(2.1)	-	-	+(1.6)	+(1.7)	+(1.9)
3NAD	-	-	-	+(1.8)	+(2.0)	-	-	-	+(1.9)	+(2.1)
Fe-3NAD	-	+(0.4)	+(1.7)	+(1.7)	+(1.9)	-	-	-	+(1.9)	+(2.1)
Cr-3NAD	-	+(1.9)	+(2.1)	++(2.3)	++(2.3)	-	+(1.7)	+(2.0)	+(2.1)	+(2.2)
Mn-3NAD	-	-	+(1.8)	+(1.9)	+(2.2)	-	-	-	+(1.7)	+(1.9)

Table 5: Antifungal activity

Name of the	*Aspergellus Niger*					*Candidaalbicans*				
compound	**20%**	**40%**	**60%**	**80%**	**100%**	**20%**	**40%**	**60%**	**80%**	**100%**
2NAD	-	-	-	+	+	-	-	-	+	+
Fe-2NAD	-	-	+	++	++	-	-	+	+	+
Cr-2NAD	+	+	+	++	+++	+	+	+	++	+++
Mn-2NAD	-	-	+	+	++	-	-	+	+	++
3NAD	-	-	+	+	++	-	-	-	+	++
Fe-3NAD	-	+	+	+	++	-	-	+	+	++
Cr-3NAD	-	+	+	++	+++	+	+	++	++	+++
Mn-3NAD	-	-	+	+	+	-	-	+	+	+

+ less activity, ++ moderate activity, +++ higher activity.

Antifungal activity

The synthesized ligands and complexes also screened for in vitro growth inhibitory activity against *Aspergillus Niger* and *Candida albicans.* Metal complexes show more activity than ligands. The inhibitory zones of compounds are in table 5. Fig. 5 shows difference between inhibitory zones of ligand and metal complex.

It has been observed from the results that the metal complexes have higher activity than the free ligands. This is probably due to the greater lipophilic nature of the complexes. Such increased activity of the metal chelates can be explained on the basis of overtone's concept and chelation theory. According to overtone's concept of cell permeability the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials due to which liposolubility is an important factor which controls the antimicrobial activity. On chelation, the probability of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donar groups. Further, it increases the delocalization of π-electron over the whole chelate ring and enhances the lipophilicity of the complex. This lipophilicity enhances the penetration of the complex into lipid membrane and blocks the metal binding sites on enzymes of microorganisms.

CONCLUSION

A series of metal complexes of 2-nitroanilinediacetylmonoxime (2NAD), 3-nitroanilinediacetylmonoxime (3NAD) with Fe (II), Cr (III) and Mn (II) have been synthesized and characterized. All complexes exhibit octahedral geometry by involvement of azomethine nitrogen and oxime oxygen of both the ligands in complex formation.All the compounds and ligands have been screened for antibacterial and antifungal activity. Compounds have exhibited promising antifungal activity and lower antibacterial activity. The complex Cr-2NAD.$2H_2O$ crystallizes in the triclinic system.

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