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Chromium(III), Manganese(III) and Iron(III) Complexes of Macrocyclic Schiff bases derived from 2,6-diaminopyridine and β-diketones

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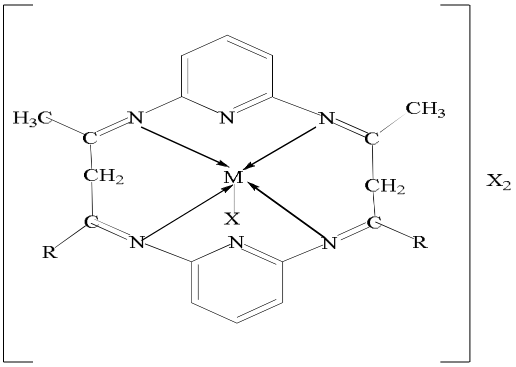
ABSTRACT

A new series of trivalent chromium, manganese and iron complexes with Macrocyclic Schiff bases, have been prepared by the in-situ synthesis of 2, 6-diaminopyridine and β-diketones, of the type $[MX(mac.)]X_2$, *[M = Cr(III), Mn(III) or Fe(III); mac = macrocyclic Schiff base] in ethanol. The complexes were characterized by analyses, electrical conductance, magnetic moment and spectral (UV-Vis, IR, and* ^1H *NMR) data. Tentative structures of the complexes have been proposed. The antifungal activities of the complexes were evaluated against Aspergillus niger, Colletotrichum falcatum and Curvularia pallescence. Manganese(III) complexes show maximum activity as compared to other metal ion complexes.*

Graphical Abstract



Keywords: Schiff bases, Chromium, Manganese, Iron, UV-Vis, IR, Antifungal activity.

INTRODUCTION

The synthetic challenge, exceptional kinetics and the possible use as models for systems of biological interest has contributed to the prominence of the coordination chemistry of macrocycles [1-3]. The reactivity and biological importance of synthetic macrocyclic complexes, especially those of azamacrocycles, continue to promote interest in the design of new complexes [4].

The reactions of metal ions by a macrocyclic ligands and modification of the resulting complexes controlled to a large extent is governed by a match between the size of a ligand hole and that of the metal ion [5]. The very high thermodynamic stability and extreme kinetic inertness of transition metal complexes polyazamacrocyclic ligands are significant since they enhance a number of important industrial applications [6-8].

There has been considerable activity concerned with the synthesis of cyclic systems, which also contain appended side chains incorporating additional donor functions [9]. Such products have been obtained both from structural modification of selected simple rings as well as *via* synthetic procedure design to produce the required macrocycle directly from non-cyclic precursors [10]. Products of this type are structurally related to both the simple macrocyclic as well as the open chain ligand categories. For example, many of the complexes exhibit the kinetic inertness which is typical of cyclic system while still showing some of the coordination flexibility frequently associated with open chain ligands. Many ligands of this category offer the prospect of inducing axial metal-ion coordination even for those cases where the pendant arms incorporate weak donor functions. Coordination will be enhanced simply because the donors are held near to the metal and hence their “effective” concentration with respect to the metal is greater than their ‘true’ concentration (with respect to bulk solution) [5-10]. The use of metals as templates in such reaction has led to the synthesis of metal complexes of macrocyclic ligands. Several macrocyclic complexes have been synthesized by the template condensation and this provides an opportunity to design and study the model biological systems to understand the chemical change taking place in such cases [11-13].

Macrocyclic species based on transition metal compounds and multidentate ligands are an interesting field in chemistry and has been the subject of extensive research [14-16] due to their polluted applications in building block macrocyclic based chemistry, environmental chemistry and biomedical.

MATERIALS AND METHODS

All the chemicals used were of A.R. grade. Ethanol and other solvents were distilled before use. Metal chlorides or acetates were procured from Sigma-Aldrich and manganese (III) acetate were prepared as reported in the literature [17, 18].

Preparation of the complexes

Preparation of chromium (III), manganese (III), iron (III) complexes with macrocyclic Schiff base ligand derived from 2,6- diaminopyridine and acetyl acetone (SDA): Chromium(III) trichloride/iron (III) chloride/manganese(III) acetate (0.01 mol) dissolved in methanol (25 cm^3) was added to a refluxing methanolic solution of 2,6- diaminopyridine (0.02 mol), acetyl acetone (0.02 mol) containing 5 cm^3 of glacial acetic acid. The resulting mixture was boiled under reflux for 24-28 h. Coloured precipitate was separated out. The precipitate was filtered off, washed with methanol and ether and dried in *vacuo*. The complexes were identified to be $[M(L)X_2]X$ (M = Cr, Mn, Fe and X = Cl or CH_3COO). Yield 50-55%. The physical properties and analytical data are given in table 1.

Characterization of metal complexes: The melting points of metal complexes were determined by open capillary method and are uncorrected. C, H and N analyses were carried out at B.H.U., Varanasi. Metals were estimated gravimetrically. The IR spectra of the ligands and complexes were recorded in the range 4000-200 cm^{-1} in potassium bromide medium on Matson 1000 model FTIR spectrophotometer and Beckman Acculab-9 spectrometer model 2000. The ^{1}H NMR spectra of ligands and few complexes were recorded in DMSO-d_6 on JEOL Al 300 spectrometer at the sweep width of 900 Hz and a sweep time of 300 sec. Chemical shifts are expressed relative to an internal references TMS (1% by volume). Magnetic susceptibility measurements were made by the Faraday method using ferrous ammonium sulphate as calibrant.

Table 1. Analytical data of chromium(III), manganese(III), iron(III) and cobalt(III) complexes with Schiff bases derived from 2,6-diaminopyridine and β-diketone

Complex	Mol. formula	Color	Yield (%)	Conductance	Analysis Found (Calcd) %			
					C	H	N	M
$[Cr(SDA)Cl_2]Cl$	$[Cr\ (C_{20}H_{22}N_6Cl_3)]$	Greenish brown	55	135	47.50 (47.59)	4.30 (4.39)	16.60 (16.65)	10.20 (10.30)
$[Mn(SDA)(OAc)_2]OAc$	$[\ Mn(C_{26}H_{32}N_6O_6)]$	Brown	52	140	53.90 (53.98)	5.00 (5.40)	14.43 (14.53)	9.40 (9.50)
$[Fe(SDA)Cl_2]Cl$	$[Fe\ (C_{20}H_{22}N_6Cl_3)]$	Brown	50	125	47.10 (47.23)	4.25 (4.36)	16.42 (16.52)	10.90 (11.00)
$[Cr(SDB)Cl_2]Cl$	$[Cr\ (C_{30}H_{26}N_6Cl_3)]$	Greenish brown	50	130	57.20 (57.29)	4.40 (4.49)	14.32 (14.43)	8.83 (8.93)
$[Mn(SDB)(OAc)]OAc$	$[\ Mn(C_{34}H_{32}N_6O_4)]$	Brown	48	138	63.40 (63.45)	4.90 (5.00)	13.00 (13.06)	8.44 (8.54)
$[Fe(SDB)Cl_2]Cl$	$[Fe\ (C_{30}H_{26}N_6Cl_3)]$	Brown	45	128	56.90 (56.94)	4.00 (4.14)	13.18 (13.28	8.80 (8.82)

SDA = Schiff base derived from 2,6-diaminopyridine and acetyl acetone, SDB = Schiff base derived from 2,6-diaminopyridine and benzoylacetone

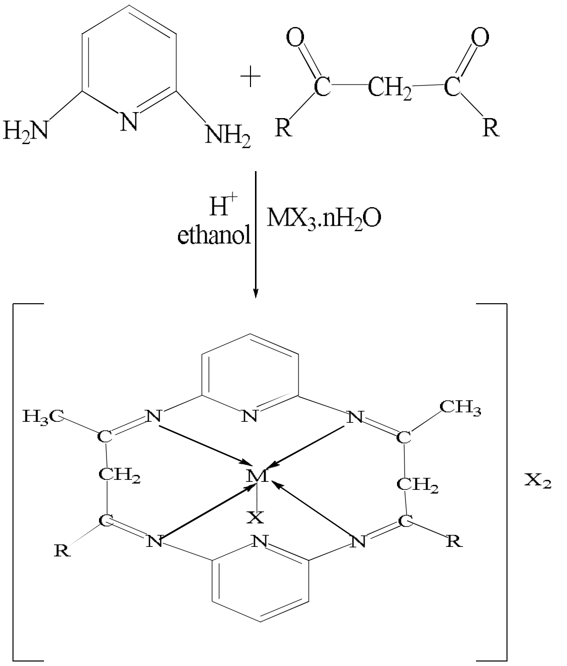
For antifungal activity, all compounds were tested against all the test fungi by the food poison technique at three concentrations (10, 100 and 1000 mg L^{-1}). For this, the desired amount of chemical was dissolved in 0.5 M of acetone and mixed with the culture medium on the basis of the volume of the medium in each petri plate (about 100 mm diameter). Oatmeal-agar medium were used for all the test fungi. In controls, the same amount of medium containing the requisite amount of solvent was poured in place of the test chemicals. A mycelia disk (5 mm diameter) obtained from the periphery of 2-week-old cultures was taken and transferred to the center of each petriplates. Plated were incubated for 7 days at 28± 2°C. Each treatment was repeated three times, and the inhibition was recorded relative to percent mycelial inhibition calculated using the formula: dc-dt/dc × 100 where dc is the average diameter of the mycelia l colony of the control and dt is the average diameter of the mycelia colony of the treatment.

RESULTS AND DISCUSSION

Synthesis of a new series of tetra dentate macrocyclic chromium(III), manganese(III), and iron(III) complexes prepared by the *in-situ* synthesis of 2,6-diaminopyridine, acetyl acetone/benzoylacetone and metal ions in 2:2:1 molar ratio, respectively, have been carried out in ethanol, which leads to the formation of $[MX(mac)]X_2$, [M = Cr(III), Mn(III) or Fe(III); mac = macrocyclic Schiff base] type complexes as shown below

All complexes are coloured solid, soluble in dimethyl formamide and dimethylsulphoxide. The electrical conductance measurements in DMF reveal these to be electrolytic in nature (125-140 ohm^{-1} cm^2 mol^{-1}). The physical properties and analytical data of the complexes are given in table 1. An attempt has also been made to prepare cobalt (III) macrocyclic Schiff base complexes by the oxidation of cobalt (II) with H_2O_2 but no success has been achieved. Blackish brown slicky products insoluble in all solvents were obtained.

Magnetic moments and Electronic spectra: Magnetic moment of chromium(III) complexes were found in the range of 4.20-4.50 B.M. These values of magnetic moment support the predicted geometry of the complexes [19]. The electronic spectra of chromium complexes show bands at *ca.* 9030-9250, 13020-13350, 17450-18320, 27435-27840 and 34820 cm^{-1}. However, these spectral bands cannot be interpreted in terms of four or six coordinated environment around the metal atom. In turn, the spectra are comparable to that of five coordinated Cr (III) complexes, whose structure has been confirmed with the help of X-ray measurements [20]. Thus keeping in view, the analytical data and 1:2 ionic nature of these complexes, a five coordinated square pyramidal geometry may be assigned for these complexes. Thus assuming the symmetry C_{4V} for these complexes [21], the various spectral bands may be assigned as$^4B_1 \longrightarrow {}^4E^a$, $^4B_1 \longrightarrow {}^4B_2$, $^4B_1 \longrightarrow {}^4A_2$, and $^4B_1 \longrightarrow {}^4E^b$. The complexes do not have idealized C_{4v} symmetry but it is being used as approximation in order to try and assign the electronic absorption bands.



[M = Cr(III) or Fe(III), X = Cl; M = Mn(III) X = CH_3COO]

The reactions may be represented by the following equation:

$$MX_3.nH_2O + 2,6\text{–DAP} + \beta\text{-diketone} \longrightarrow [MX(mac)]X_2$$

[M = Cr(III), Mn(III) or Fe(III); mac = macrocyclic Schiff base]

The magnetic moment of manganese (III) complexes were found to be 4.80-4.85 B. M. The electronic spectrum of manganese complexes shows three d-d bands at approximately 12.250, 16.045, and 35.435 cm^{-1}. The higher energy band at 35465 cm^{-1} may be assigned due to charge transfer transitions. The spectrum resembles those reported for five-coordinate square pyramidal manganese porphyrins [21]. This idea is further supported by the presence of the broad ligand field band at 20410 cm^{-1} diagnostic of C_{4v} symmetry and thus the various band may be assigned as follows $^5B_1 \longrightarrow {}^5A_1$, $^5B_1 \longrightarrow {}^5B_2$, and $^5B_1 \longrightarrow {}^5E$, respectively. The band assignment in single electron transition may be made $d_z{}^2 \longrightarrow d_{x^2-y^2}$, $d_{xy} \longrightarrow d_{x^2-y^2}$ and d_{xy}, $d_{yz} \longrightarrow d_{x^2-y^2}$, respectively, in order to increasing energy. However, the complexes do not idealized C_{4v} symmetry.

Magnetic moment of iron (III) complexes lie in the range 5.82-5.90 B.M. and are in accordance with proposed geometry of the complexes. The electronic spectra of trivalent iron complexes show various bands 9825-9975, 15525-15570, 27635-27710 cm^{-1}, and these band do not suggest the octahedral or tetrahedral geometry around the metal atom. The spectral bands are consistent with the range of spectral bands reported for five coordinate square pyramidal iron(III) complexes [22]. Assuming C_{4V} symmetry for these complexes, the various bands can be assigned as $d_{xy} \longrightarrow dxz$, $d_{yz}$and d_{xy}, $\longrightarrow dz^2$. Any attempt to make accurate assignment is difficult due to interaction of the metal-ligand π-bond systems lifting the degeneracy of the d_{xz} and d_{yz} pair.

Infrared spectra: The infrared spectrum of 2,6-diaminopyridine, show bands at *ca.* 3260 cm^{-1} and 3200 cm^{-1} corresponding to $\nu(NH_2)$ but are absent in the IR spectra of complexes. Further, no strong absorption band was observed near 1700 cm^{-1} as observed in the spectra of β-diketones indicating the absence of C=O group of diketones. This confirms the condensation of carbonyl groups of β-diketone with amino groups of 2,6-diaminopyridine [17]. This fact is further supported by appearance of a strong absorption band in the region 1600-1580 cm^{-1} in the IR spectra of all complexes which may be attributed to ν(C=N). These results provide strong evidence for the formation of macrocyclic frame [23]. The lower value of ν(C=N) indicates the coordination of nitrogen of azomethine to metal ion [18]. The far infrared spectra show bands in the region *ca.* 300-315 cm^{-1} are assigned to ν(M-Cl) (M = Cr or Fe) vibrations. The presence of coordinated acetate group in manganese (III) complexes is confirmed by the appearance of medium band at *ca.* 1520 cm^{-1} and a strong band at *ca.* 1480 cm^{-1}. In addition the complexes show bands at *ca.* 1560, 670 and 400 cm^{-1}, assignable to pyridine ring deformation bands. These bands almost appear at same frequencies as in 2,6-diaminopyridine. A large no. of bands also arise due to phenyl ring and different alkyl groups but definite assignments of these bands are not possible due to the complexity of the spectrum arising out of the overlap of these absorptions.

APPLICATION

All the ligands and their corresponding complexes were screened in-vitro for their antifungal activity against *Aspergillus niger, Colletotrichum falcatum* and *Curvularia pallescence.* The results of antifungal screening are present in table 2. The activity was compared with those of the standard drug fluconazole. Any particular species of fungus, manganese(III) derivatives show better activity than iron(III) derivatives. Chromium(III) complexes show least activity as compared to manganese(III) and iron(III) derivatives. The activity of the ligands is affected by the nature of the substituents, this in relation to the lipophilicity of the ligands and their membrane permeability, a key factor in determining their entry inside the cell. The presence of –Cl or –OCH_3 group at the phenyl rings of the ligands increases the activity of the derivatives. The activity decreases on dilution.

Table 2. Fungicidal screening data of Cr(III), Mn(III), Fe(III) and Co(III) complexes of Schiff bases derived from 2,6-diaminopyridine and β-diketone

S.No	**Compound**	**Fungicidal Inhibition (%)**								
		Aspergillus niger			***Colletotrichum falcatum***			***Curvularia pallescence***		
		10 ppm	**100 ppm**	**1000 ppm**	**10 ppm**	**100 ppm**	**1000 ppm**	**10 ppm**	**100 ppm**	**1000 ppm**
1	[Cr(SDA) Cl_2]Cl	32.4	31.9	33.5	32.8	32.9	33.8	33.1	32.8	34.5
2	[Mn(SDA) $(OAc)_2$]OAc	35.0	37.5	40.5	35.3	37.6	41.5	35.8	37.9	42.0
3	[Fe(SDA)Cl_2]Cl	33.2	34.6	35.5	33.4	34.7	36.5	33.8	34.9	37.5
4	[Cr(SDB) Cl_2]Cl	31.2	32.4	38.0	31.6	33.4	39.2	32.4	34.2	39.5
5	[Mn(SDB) (OAc)]OAc	34.4	35.6	39.8	34.5	35.9	40.1	35.2	35.1	40.2
6	[Fe(SDB)Cl_2]Cl	32.8	33.5	34.8	33.1	34.2	35.2	33.5	34.6	35.6

SDA = Schiff base derived from 2,6-diaminopyridine and acetylacetone, SDB = Schiff base derived from 2,6-diaminopyridine and benzoylacetone

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