Spectrochimica Acta Part A 79 (2011) 272–277

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, spectroscopy and biological investigations of manganese(III) Schiff base complexes derived from heterocyclic β-diketone with various primary amine and 2,2′-bipyridyl

Kiran R. Surati*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388120, Anand, Gujarat, India

ARTICLE INFO

Article history:
Received 25 September 2010
Received in revised form
21 December 2010
Accepted 7 March 2011

Keywords:
Spectroscopy
Manganese(III) complexes
Thermal behaviour
Antimicrobial

ABSTRACT

The mixed ligand mononuclear complex [Mn(bipy)(HPMFP)(OAc)]ClO_4 was synthesized by reaction of $Mn(OAc)_3{\cdot}2H_2O$ with HPMFP and 2,2′-bipyridyl. The corresponding Schiff base complexes were prepared by condensation of [Mn(bipy)(HPMFP)(OAc)]ClO_4 with ethylenediamine, ethanolamine and glycine (where HPMFP = 1-phenyl-3methyl-4-formyl-2-pyrazolin-5one, bipy = 2,2′-bipyridyl). All the compounds have been characterized by elemental analysis, magnetic susceptibility, conductometry measurements and ^1H and ^{13}C NMR, FT-IR, mass spectrometry. Electronic spectral and magnetic susceptibility measurements indicate square pyramidal geometry around manganese(III) ion. The thermal stabilities, activation energy E^*, entropy change ΔS^*, enthalpy change ΔH^* and heat capacity of thermal degradation for these complexes were determined by TGA and DSC. The *in vitro* antibacterial and antifungal activity of four coordination compounds and ligand HPMFP were investigated. *In vitro* activates of *Bacillus subtillis* (MTCC-619), *Staphylococcus aureus* (MTCC-96), *Escherichia coli* (MTCC-722) and *Klebsiella pneumonia* (MTCC-109) bacteria and the fungus *Candida albicans* (ATCC-90028) were determined. All the compounds showed good antimicrobial activity. The antimicrobial activities increased as formation of Schiff base.

1. Introduction

The chemistry of pyrazolone derivatives has attracted scholarly attention because of its structures and application in diverse areas [1–4]. Pyrazolone are key structure in numerous compound of therapeutic importance [5], compounds containing this ring system are known to display diverse pharmacological activities such as inhibitors of mycobacterium tuberculosis [6], potent activity of inhibiting protease-resistant prion protein accumulation [7], anti-tumor necrosis factor activity [8,9] and inhibition of human telomerase [10]. Recently Botta et al. reported synthesis, biological evaluation and structure–activity relationship (SAR) analysis of this class of compounds [11]. Recently many other researchers are extensively working on pyrazolone based coordination compounds and its antibacterial and anticancer activity [12,13]. Caruso et al. [14] reported the synthesis, structure, and antitumor activity of coordination complex cyclo-tetrakis[bis(1-phenyl-3-methyl-4-benzoylpyrazolone-5-ato)μ-oxotitanium(IV)]. The antitumor activity of this compound, encapsulated in a dipalmitoylphosphatidylcholine liposome, has been reported *in vitro* and in vivo using tumor cell lines. Recently Liguori et al. reported the non classical anticancer agents and its synthesis and biological evolution of Zn(II) complexes derived from N,N-chelating ligands (4,4′-dinonyl-2,2′-bipyridine) and diketonates [15]. Due to large diversity and importance of pyrazolone based compounds many reviews available to explore the chemistry of pyrazolone, structures and its applications [16,17].

Manganese(III) complexes have also merited much attention in the field of biological study and application [18,19]. Recently Pandya et al. reported the synthesis, characterization and antibacterial activity of Schiff base pyrazolone derivatives with transition metal ions [20].

Taking into account of manganese(III), pyrazolone base compounds and their therapeutic importance, here we use pyrazolone derivatives as chelating agent with biologically rich transition metal ion manganese(III). All these reports encouraged us to study the coordination chemistry and biological behaviour of Schiff base complexes of manganese(III) though there are fewer studies on the biological activities of manganese(III) Schiff base complexes derived form pyrazolone based moiety.

Our interest in this area is focused for a considerable time on the investigation of coordination chemistry of transition metal with using pyrazolone based ligand [21–26]. To gain more infor-

* Tel.: +91 09904368680; fax: +91 02692 236475.
E-mail address: kiransurati@yahoo.co.in

1386-1425/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2011.03.008

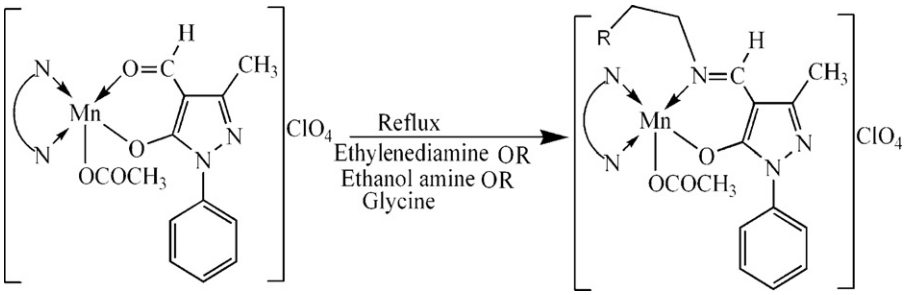

Fig. 1. General structure of Schiff base Mn(III) complexes.

mation about the structure and stereochemistry of such type of complexes, a detailed investigation on a new mono and binuclear manganese(III) complexes with a ligand involving imine-nitrogen, phenolic oxygen as donors has been initiated on our part [23].

In present work, we report here the synthesis and characterization of Schiff base complexes of manganese(III) derived from the mononuclear mixed ligand complexes [23]. All the compounds tested and discussed their *in vitro* activates with bacteria *Bacillus subtillis* (MTCC-619), *Staphylococcus aureus* (MTCC-96), *Escherichia coli* (MTCC-722) and *Klebsiella pneumonia* (MTCC-109) and the fungus *Candida albicans* (ATCC-90028).

2. Experiment

The solvents were used after purification by the standard method described in the literature [27,28]. 1-Phenyl-3-methyl-2-pyrazoline-5-one (E-Merck); ethylenediamine (BDH); and ophenylenediamine (Fluka A.G., Switzerland) were used as received. $Mn(OAc)_3{\cdot}2H_2O$ was prepared by the oxidation of $[Mn_3(\mu_3\text{-}O)(OAc)_6(H2O)_3]{\cdot}3H_2O$ using Gündüz's method [29]. 1-Phenyl-3methyl-4-formyl-2-pyrazolin-5-one was synthesized and characterized previously [25,30] by condensation of 1-phenyl 3-methyl-2-pyrazoline 5-one with DMF and $POCl_3$.

Elemental analyses (C, H, N) were performed at CDRI, Lucknow. Solid-state infrared spectra were recorded with a Perkin-Elmer IR spectrophotometer using KBr pellets at SICART, Vallabh Vidyanagar, Anand. ^1H and ^{13}C NMR spectra were recorded with JEOL-GSX-400 using $CDCl_3$ as a solvent and TMS as an internal reference at Department of Chemistry, S.P. University, Anand. Mass spectra (EI) were obtained on a JEOL D-300 mass spectrometer at SAIF, IIT Madras, Chennai. The FAB mass spectra were recorded on a JEOL SX 102 mass spectrometer using Argon/Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature by using *m*-nitrobenzyl alcohol (NBA) as matrix. Electronic spectra in the 200–800 nm range were obtained in acetone on "SHIMADZU" UV 160A using quartz cell of 1 cm^3. Magnetic measurements were carried out at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant at Department of chemistry, Vallabh Vidyanagar, Anand. Molar conductance of the mixed ligand Schiff base complexes was measured on Systronics direct reading conductivity meter type CM-82T. TGA/DTA was carried out on universal V3.0G TA instrument in the range 0–700 °C at a heating rate of 10 °C/min under nitrogen at Department of Chemistry, Vallabh Vidyanagar, Anand. DSC was carried out on universal V3.0G TA instrument in the range 0–300 °C at Department of Chemistry, Vallabh Vidyanagar, Anand.

2.1. Preparation of the mononuclear mixed ligand complex

2.1.1. Preparation of Schiff base complexes

The Schiff base complexes were prepared by 1:1 interaction of mixed ligand complex and ethylenediamine ethanolamine or glycine (Fig. 1).

To the mixed ligand complex of Mn(III) (7.12 g, 0.0125 mol) 25 cm^3 methanol was added ethylenediamine (0.75 g, 0.0125 mol), ethanolamine (0.76 g, 0.0125 mol) or glycine (0.93 g, 0.0125 mol). The solution was allowed to stand for 10 min at room temperature and then refluxed for 2 h on a water bath. The solution was reduced to 1/3 volume and allowed to stand overnight at room temperature. A solid mass separated, was collected and washed by ether. Crystallization was done with methanol and the complexes dried over $CaCl_2$ (Fig. 2).

2.2. Microbiological studies

2.2.1. Test microorganism and medium

The bacterial subcultures for *B. subtillis* (MTCC-619), *S. aureus* (MTCC-96), *E. coli* (MTCC-722) and *K. pneumonia* (MTCC-109) were obtained from central diagnostic laboratory, Surat, Gujarat, India. An antifungal susceptibility test was used *C. albicans* (ATCC-90028). *S. aureus*, *E. coli*, *K. pneumonia* and *C. albicans* were cultured on Brain Heart Infusion Broth (BHI) for the antibacterial and antifungal activity.

2.2.2. Method

The compounds were tested for their antimicrobial activity by the minimum inhibitory concentration (MIC) [31] of mononuclear complexes and their corresponding Schiff base complexes of Mn(III). Each compound was dissolved in DMF or DMSO or appropriate solvent at different concentrations of 2.5, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 μg/mL. The solutions of standard drug, Streptomycin was prepared in the same concentrations. Inoculums of the bacterial culture were prepared. To a series of tubes containing 1 mL each of Mn(III) complexes solution with different concentrations and 0.2 mL of inoculum was added. Further 4.0 mL of the sterile water was added to each of the test tubes. These test tubes

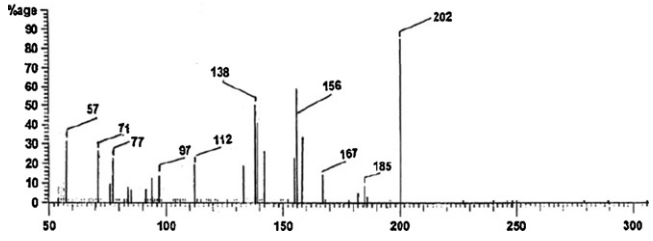

Fig. 2. Mass spectra of ligand PMFP.

Table 1
Analytical and physical data of PMFP ligand and Schiff base complexes.

Compounds	Colour (% yield)	m.p./°C	Elemental analysis; experimental (calculated) %					μ_{eff}/B.M.	Conductance/ Ω^{-1} cm^2 mol^{-1}
			C	H	N	Mn	Cl		
Ligand HPMFP($C_{11}H_{10}N_2O_2$)	Yellow	176	65.92 (65.3)	5.04 (4.9)	12.97 (13.0)	–	–	–	–
[Mn(PMFP)(dipy)(OAc)]ClO_4 ($C_{23}H_{20}MnN_4O_8Cl$)	Brown	193	48.30 (48.38)	3.50 (3.53)	9.80 (9.82)	9.61 (9.62)	6.20 (6.21)	5.02	107
[Mn(PMFP-en) (dipy) (OAc)]ClO ($C_{25}H_{26}MnN_6O_7Cl$)	Brown	166	48.91 (48.98)	4.23 (4.28)	13.69 (13.71)	8.95 (8.96)	5.81 (5.78)	4.97	116
[Mn(PMFP-EA) (dipy)(OAc)]ClO_4 ($C_{25}H_{25}MnN_5O_8Cl$)	Brown	172	48.43 (48.90)	4.03 (4.10)	11.30 (11.41)	8.87 (8.95)	5.80 (5.78)	5.03	122
[Mn(PMFP-Gly) (dipy)(OAc)]ClO_4 ($C_{25}H_{26}MnN_5O_9Cl$)	Dark brown	192	47.74 (47.73)	3.66 (3.56)	11.14 (11.15)	8.75 (8.64)	5.60 (5.65)	5.10	126

were incubated for 24 h and observed for presence of turbidity. This method was repeated by changing compounds with standard drug (Streptomycin) for comparison. The minimum inhibitory concentration at which no growth was observed was taken as the MIC values.

3. Results and discussion

The newly synthesized ligand PMFP and their mixed ligand complexes were stable. They were soluble in organic solvents like methanol, ethanol, acetone, DMF and DMSO. The analytical data agreed were in good agreements with the proposed structure of ligand and its mixed ligand complexes (Table 1).

3.1. NMR spectra

×The ^{1}H NMR spectrum of ligand shows a broad singlet at δ 8.49 ppm due to –OH proton, indicating that the ligand is in the enol form [24]. The spectrum also shows the phenyl multiple at δ 7.3–7.9 ppm, a sharp singlet at δ 1.2 ppm assigned to methyl protons of the pyrazoline ring, and the aldehyde proton at 9.85 ppm. HPMFP is in the enol form only. The ^{13}C NMR spectrum of ligand show characteristic peck for C3, C4 and C5 due to which pyrazolone ring carbon atoms resonates at δ 131.5, 110.2 and 152.4. The formation of aldehyde was confirmed with the carbon resonate at δ 192.1 for C=O. Other phenyl ring and methyl carbon atoms are observed in the range of δ 121.1–126.5 and 8.1 respectively.

3.2. Infrared spectra

The IR spectra of ligand show characteristics band at 3400–3300 cm^{-1} due to υ(OH). Free υ(OH) is generally observed at 3500–3600 cm^{-1}; the observed lower value is due to intramolecular and intermolecular H-bonding [24,25]. The IR spectrum of the lignad shows doublet at 2755 and 2816 cm^{-1} (Fermi resonance) assigned to the aldehydic υC–H, whereas two moderately intense bands are observed at 3020 cm^{-1} and 2877 cm^{-1}, due to aromatic and aliphatic υC–H respectively. The very sharp absorption band appeared at 1624 cm^{-1} is assigned to υC=O which is shifted to lower wave number because of intramolecular hydrogen bonding. The pyrazoline ring υC=N and υC=C are observed at 1541 cm^{-1} and 1510 cm^{-1} respectively. The bands observed at 1397 cm^{-1} and 794 cm^{-1} can be assigned to in-plane and out of plane bending modes of aldehydic C–H [32]. The medium-sharp band observed at 845 cm^{-1} is attributed to out-of-plane bending of the bonded –OH group. All the data indicate that the PMFP is an enol form only.

The FT-IR spectral data of the Mn(III) mononuclear complex and the Schiff base complexes are given in Table 2. The Mn(III) mononuclear mixed ligand complexes does not show a band between 3600 and 3400 cm^{-1} indicating the –OH hydrogen of PMFP at the fifth position is deprotonated after complexation. A new band in all complexes at 1328–1353 cm^{-1} is due to the enolic group υC–O [25,33]. On coordination υC=N shifts to lower wavenumber 1600–1620 cm^{-1} from 1640 to 1660 cm^{-1} for free C=N. The band at 3320 cm^{-1} show that NH_2 group of ethylendiamine Schiff-base complex is not coordinated to the metal ion. The sharp band at 3515 cm^{-1} in ethanolamine complex of Mn(III) correspond to free –OH of ethanolamine. In the glycine complex broad bands at 3350–3100 cm^{-1} and 1666 cm^{-1} are assigned for undissociated carboxylic group of glycine. In all the complexes, a weak band is obtained at 1566–15491 cm^{-1} region. This may be due to asymmetric COO stretching of the acetate group. The symmetric COO stretching band appeared at 1433–1423 cm^{-1} region [33,34]. The presence of counter ion perclorate (ClO_4^-) is confirmed through a weak band at 914 cm^{-1} due to the symmetrical stretching mode (IR-forbidden) and an asymmetrical stretching mode at 1100 cm^{-1} (IR-allowed). This shows that (ClO_4^-) has T_d symmetry [25,35,36].

3.3. Magnetic measurement

The magnetic moment of the mononuclear mixed ligand complex and its Schiff base complexes of Mn(III) show μ_{eff} in the range 4.97–5.10 B.M., indicating that Mn(III) chelates are high spin d^4 configuration (t_{2g}^3, eg^1). This value is expected for four unpaired electrons and lack of any kind of exchange interaction [23].

Table 2
FT-IR and electronic spectral data of complexes and their assignments.

Complex	υCOO Str.	υC=N coord.	υC=N (cyclic)	υC–O Str.	d–d (cm^{-1})	Charge transfer band (cm^{-1})
[Mn(PMFP)(dipy)(OAc)]ClO_4	1566, 1360	–	1593	1353	23,529	48,543, 41,034
[Mn(PMFP-en) (dipy) (OAc)]ClO_4	1550, 1368	1600	1596	1328	25,063, 20,080, 13,559	42,016, 36,496
[Mn(PMFP-EA) (dipy)(OAc)]ClO_4	1549, 1368	1620	1598	1353	26,343, 13,568	42,372, 36,101
[Mn(PMFP-Gly) (dipy)(OAc)]ClO_4	1550, 1369	1609	1599	1353	26,666	42,372, 36,231

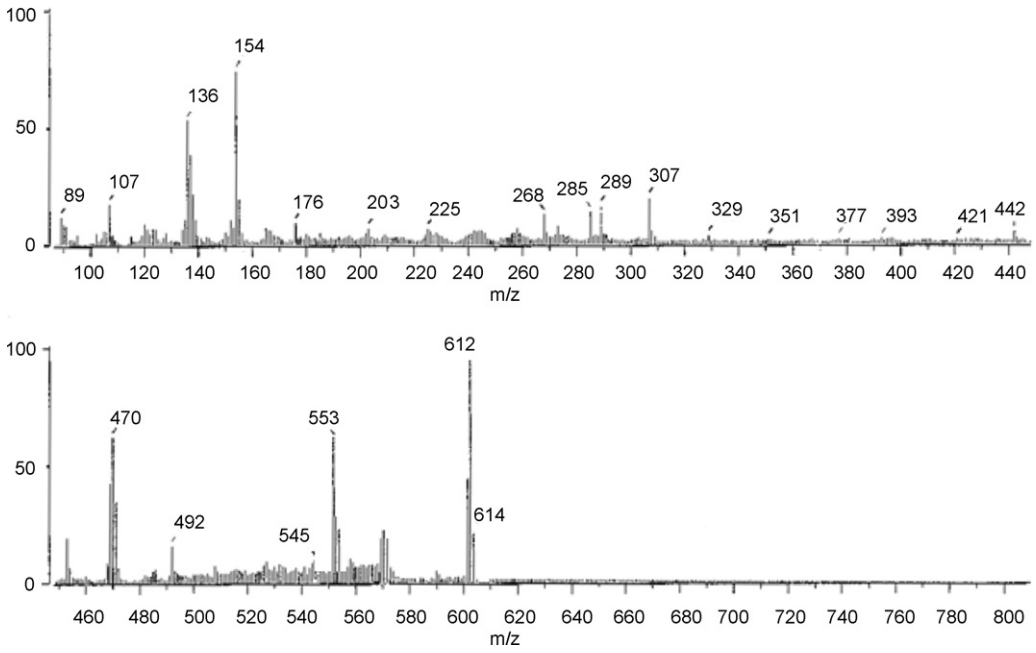

Fig. 3. Mass spectra of Schiff base complex [Mn(PMFP-en) (dipy) (OAc)]ClO_4.

3.4. Electronic spectra

UV–visible spectra of mononuclear manganese(III) complexes and their Schiff base complexes were carried out in methanol. The data are summarized in Table 2.

The absorption spectra of mononuclear mixed ligand complexes show an intense band at 36,496 cm^{-1} and 23,502 cm^{-1} due to interligand transition and d–d transition respectively. The absorption spectra of Schiff base chelates exhibit (LMCT) band between 33,445 and 36,496 cm^{-1} whereas d–d transition at 25,063, 20,080, 13,559 cm^{-1}, 18,182 cm^{-1} and 23,809 cm^{-1}, 13,559 cm^{-1} in ethylenediamine, ethanolamine and glycine Schiff base complexes respectively. These can be assigned to $^5B_1 \rightarrow {}^5E(\upsilon_3)$, $^5B_1 \rightarrow {}^5B_2(\upsilon_2)$ and $^5B_1 \rightarrow {}^5A_2(\upsilon_1)$ respectively. Since, Mn(III) ion is easily reducible, charge transfer will be from ligand to metal (LMCT) correspond to $\pi \rightarrow t_2$ transition [21,35]. Keeping in view the monoanionic, bidentate nature of PMFP and their Schiff base ligands, bidentate nature of 2,2′-dipyridyl and monodentate coordinating behaviour of the acetate group, a square-pyramidal structure seems to be the most probable one. It is further evidenced by the presence of a ligand field band around 18,000–20,000 cm^{-1} diagnostic of C_{4V} symmetry [37].

3.5. Mass spectra

Mass spectra of all the compounds stand in good agreement with proposed structure, the representative mass spectra shown in Figs. 3 and 4. The EI mass spectra of ligand PMFP and FAB mass spectra of Schiff base complexes [Mn(PMFP-en) (dipy) (OAc)]ClO_4 are carried out. Cleavage taking place in the HPMFP ligands and fragments observed were in good agreement with structure of ligand [38,39]. Here the molecular ion peak and base peak at 202 m/z is same, which is confirmed from abundance of molecular ion peak [39].

PMFP is characterized by mass spectral studies with a molecular ion peak at 202(M^+). A weak peak at m/e 201 is due to the formation of $(C_{11}H_9N_2O_2)^+$, elimination of H from the molecule. One intense peak at m/e 185 is due to removal of OH and formation of $(C_{11}H_8ON_2)^+$, a distinct but less abundant peak observed at (m/e = 174) due to elimination of CO from the parent compound. Prominent peaks for $(C_6H_5N)^+$ and $(C_6H_5)^+$ ions are observed at m/e = 91 and 77. Molecular mass of all the metal complexes performed with FAB mass spectrometer. A FAB mass spectrum (Fig. 4) of representative complex [Mn(PMFP-en) (dipy) (OAc)]ClO_4 was recorded. The Schiff base complexes [Mn(PMFP-en) (dipy) (OAc)]ClO_4 shows characteristic molecular ion peak at m/z = 612 $[M]^+$. One other peak observed at m/z = 614 $[M+2]^+$ may be due to isotopic abundance peak for Cl atom. The peak observed at 571 m/z and 470 m/z are due to removal of fragment acetate (OAc) and 2,2′-bipyridine respectively. Other fragments are in good agreement with the complexes structure [21,25].

3.6. Thermogravimetric analysis

The thermal study of complexes and its kinetic parameter were determined. The kinetics of heterogeneous condensed phase reactions that occur under nonisothermal conditions is usually

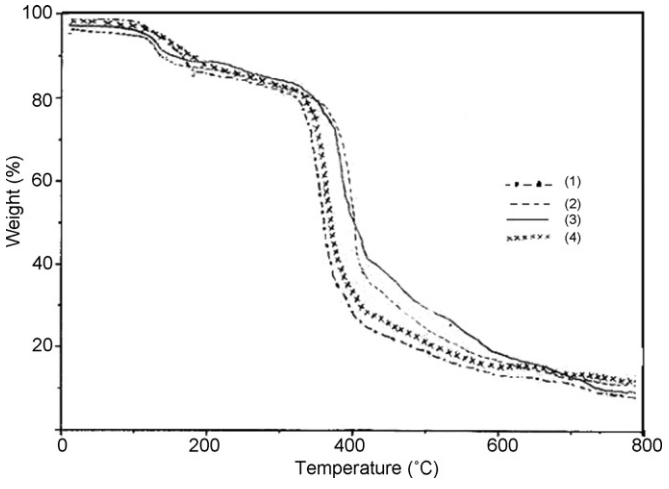

Fig. 4. Thermal analyses of Mn(III) complexes where (**1** = [Mn(PMFP) (dipy)(OAc)]ClO_4; **2** = [Mn(PMFP-en) (dipy) (OAc)]ClO_4; **3** = [Mn(PMFP-EA) (dipy)(OAc)]ClO_4; **4** = [Mn(PMFP-Gly) (dipy)(OAc)]ClO_4).

Table 3
The TG data for mononuclear Mn(III) complexes and its Schiff base complexes.

Complex	First step/°C	Mass loss, Δm found/(calc.) %	Second step/°C	Mass loss, Δm found/(calc.) %	Residue	Calc. (found) %
[Mn(PMFP)(dipy)(OAc)]ClO_4	129.6–184.0	9.18 (10.3)	216.5–488.46	80.72 (82.94)	MnO_2	13.21(15.25)
[Mn(PMFP-en) (dipy) (OAc)]ClO_4	128.1–190	10.12 (9.64)	240.2–465.9	81.28 (84.27)	MnO_2	12.26 (14.28)
[Mn(PMFP-EA) (dipy)(OAc)]ClO_4	129.0–198.0	9.92 (9.52)	258.1–476.9	80.10 (84.26)	MnO_2	15.14 (14.03)
[Mn(PMFP-Gly) (dipy)(OAc)]ClO_4	131.1–188.6	11.2 (9.38)	228.1–484.0	81.29 (84.85)	MnO_2	15.28 (13.83)

Table 4
Kinetic data of the thermal decomposition of Mn(III) complexes.

Complex	C_p/J g^{-1} °C^{-1}	T_S/°C	T_1/°C	T_2/°C	T_P/°C	ΔH^*/kJ mol^{-1}	ΔS^*/kJ $mol^{-1}K^{-1}$	E^*/kJ mol^{-1}	C_s
[Mn(PMFP)(dipy)(OAc)]ClO_4	1.36	121.2	136.3	178.2	161.2	47.23	0.210	22.56	0.36
[Mn(PMFP-en) (dipy) (OAc)]ClO_4	1.67	128.1	148	182.76	166.16	58.10	0.132	23.40	0.31
[Mn(PMFP-EA) (dipy)(OAc)]ClO_4	1.54	129.0	149.54	195.24	172.34	70.44	0.158	28.84	0.29
[Mn(PMFP-Gly) (dipy)(OAc)]ClO_4	2.38	131.1	174.96	229.64	192..17	130.20	0.279	18.96	0.37

described by the equation [40].

$$\beta \frac{\partial \alpha}{\partial T} = A_f(\alpha) \exp\left(-\frac{E}{RT}\right)$$

where α is the degree of conversion, β is the linear heating rate, $A_f(\alpha)$ is the differential conversion function. Each step of decomposition in most of the reactions of the solids follows the trend

$$\text{Solid } 1 \xrightarrow{\text{Heat}} \text{Solid } 2 + \text{Gas}$$

This process comprises several stages, such as the chemical act of breaking of bonds, breakdown of the solid 1 crystal lattice, formation of the crystal lattice of the solid 2 [40], absorption–desorption of the gaseous products, diffusion of gas and heat transfer. The TG curves show two step degradation first removals of one coordinated acetate ion and second due to pyrolysis of organic ligand molecules. Thermal stability of the complexes evaluated from the TG curves shown in (Fig. 4) and order of stability as follows.

[Mn(PMFP-en)(dipy)(OAc)]ClO_4 > [Mn(PMFP-EA)(dipy)(OAc)]ClO_4 > [Mn(PMFP-Gly)(dipy)(OAc)]ClO_4 > [Mn(PMFP)(dipy)(OAc)]ClO_4

From DSC it is confirmed that the complexes exhibited an endothermic process. The area of the endothermic peak corresponding to the heat of fusion and the peak temperature corresponds to the melting point. The melting (T_p), transition temperature (T_1, T_2), heat of reaction (ΔH), and entropy (ΔS) of the complexes were calculated from DSC results and are given in Table 3. The heat capacities C_p of the complexes were calculated from DSC results and are given in Table 3. From the TG thermal stability temperature (T_s) and removal of $-COOCH_3$ group are observed form the TG curves, further it is confirmed with DSC [25]. The final solid product of thermal decomposition is MnO_2. All the thermal decomposition and its kinetic parameter were summarized in Table 4.

3.7. Antimicrobial activities

In vitro activates of *B. subtillis* (MTCC-619), *S. aureus* (MTCC-96), *E. coli* (MTCC-722) and *K. pneumonia* (MTCC-109) bacteria and the fungus *C. albicans* (ATCC-90028) were carried out for mononuclear complex [Mn(bipy)(PMFP)(OAc)]ClO_4 and their corresponding Schiff base complexes. The susceptibilities of certain strains of bacteria and a fungus to the mononuclear complexes and their corresponding Schiff base complexes were evaluated by measuring the minimum inhibitory concentration at which no growth was observed was taken as the MIC values. The results are given in Table 5 for all the complexes. Comparison of MIC values (in μg/mL) of Mn(III) complexes and standard drugs against different bacteria are presented in Table 5.

In the literature, most of the Schiff base derivatives are reported to be more active against representative bacteria and fungus than their complexes under identical condition [41,42]. In our work, we also observed that the Schiff bases complexes are more active against bacteria and fauns. From these results, it is evident that [Mn(PMFP-Gly)(dipy)(OAc)]ClO_4, [Mn(PMFP-EA) (dipy)(OAc)]ClO_4 and [Mn(PMFP-en) (dipy) (OAc)]ClO_4 show superior activity when compared to Streptomycin and towards inhibiting all tested bacterial strains. The rest mononuclear complex [Mn(bipy)(PMFP)(OAc)]ClO_4 and ligand PMFP are less active compared with Streptomycin. It is very interesting that introduction of Schiff base (azomethine) enhance the activity against the bacteria and fungi, further it also creates the effect of metal ions on the normal cell membrane. Schiff base complexes bear polar and nonpolar properties together; this makes them suitable for permeation to the cells and tissues. Changing the hydrophilicity and lipophilicity probably leads to bring down the solubility and per-

Table 5
Minimum inhibitory concentration of the Mn(III) complexes and Streptomycin.

Complexes and standard	Range of concentration (2.5–50 μg/mL)				
	MTCC-619	MTCC-96	MTCC-722	MTCC-109	ATCC-90028
Ligand HPMFP	25	30	25	30	20
[Mn(PMFP)(dipy)(OAc)]ClO_4	20	15	20	20	15
[Mn(PMFP-en) (dipy) (OAc)]ClO_4	10	10	2.5	15	10
[Mn(PMFP-EA) (dipy)(OAc)]ClO_4	5.0	5.0	15	10	5.0
[Mn(PMFP-Gly) (dipy)(OAc)]ClO_4	2.5	2.5	10	5.0	5.0
Streptomycin (standard)	10	15	20	15	10

meability barrier of cell, which in turn enhances the bioavailability of chemotherapeutics on one hand and potentiality at another [43,44].

3.8. Molar conductance

The observed molar conductances of the manganese(III) complexes (Table 1) in 10^{-2} M DMF solution are in the range 107–126 Ω^{-1} cm^2 mol^{-1}. The molar conductance values are consistent with the monoelectrolytic nature of Mn(III) complexes [45,46].

4. Conclusion

On the basis of above studies the general structure of the Mn(III) complexes are proposed as shown in Fig. 1. The Schiff base complexes having square pyramidal geometry with N, O as donor site from β-diketone and N,N contributed from the neutral ligand 2,2′-bipyridyl. Monodentate nature of anion OAc confirmed from the FT-IR and thermal study it indicates coordination with metal ion. Electronic spectra, magnetic moment and conductance study evidence the fact of square pyramidal geometry of complexes. Moreover biological screening state that Schiff base complexes enhance the activity against the bacteria and fungi due to Schiff base complexes bear polar and nonpolar properties together; this makes them suitable for permeation to the cells and tissues.

Acknowledgements

The author express their sincere thanks to University University Grant Commission (F.No. 36-368/2008 SR) for financial support and the Head, Department of Chemistry, Sardar Patel University, CDRI, Lucknow, SICART, Vallabha Vidyanagar, Anand, SAIF, IIT Chennai, SAIF, IIT Mumbai for providing instrumental facility.

References

[1] F. Marchetti, C. Pettinari, A. Cingolani, R. Pettinari, M. Rossi, F. Caruso, J. Organomet. Chem. 645 (2002) 134–145.
[2] B. Peng, G. Liu, L. Liu, D. Jia, K. Yu, J. Mol. Struct. 692 (2004) 217–222.
[3] C. Ching-Hsin, W. Fang-Iy, S. Ching-Fong, C. Chin-Hsiung, T. Yu-Tai, J. Mater. Chem. 10 (2004) 1585–1589.
[4] Y. Jinmao, S. Xiao, D. Chenxu, S. Zhiwei, S. Yourui, W. Honglun, L. Yulin, Anal. Chim. Acta 609 (2008) 66–75.
[5] F. Caruso, C. Pettinari, F. Marchetti, M. Rossi, C. Opazo, S. Kumar, S. Balwani, B. Gohsh, Bioorg. Med. Chem. 17 (2009) 6166–6172.
[6] D. Castagnolo, F. Manetti, M. Radi, B. Bechi, M. Pagano, A.D. Logu, R. Meleddu, M. Saddi, M. Botta, Bioorg. Med. Chem. 17 (2009) 5716–5721.
[7] A. Kimata, H. Nakagawa, R. Ohyama, T. Fukuuchi, S. Ohta, T. Suzuki, N. Miyata, J. Med. Chem. 50 (2007) 5053–5056.
[8] M.P. Clark, S.K. Laughlin, M.J. Laufersweile, R.G. Bookland, T.A. Brugel, A. Golebiowski, M.P. Sabat, J.A. Townes, J.C. Vanrens, J.F. Djung, M.G. Natchus, L.C. Hsieh, S.C. Xu, R.L. Walter, M.J. Mekel, S.A. Heitmeyer, K.K. Brown, K. Juergens, Y.O. Taiwo, M.J. Janusz, J. Med. Chem. 47 (2004) 2724–2727.
[9] M.J. Laufersweiler, T.A. Brugel, M.P. Clark, A. Golebiowski, R.G. Bookland, S.K. Laughlin, M.P. Sabat, J.A. Townes, J.C. Vanrens, J.F. Djung, M.G. Natchus, L.C. Hsieh, S.C. Xu, R.L. Walter, M.J. Mekel, S.A. Heitmeyer, K.K. Brown, K. Juergens, Y.O. Taiwo, M.J. Janusz, Bioorg. Med. Chem. Lett. 14 (2004) 4267–4272.
[10] Y. Kakiuchi, N. Sasaki, M. Satoh-Masuoka, H. Murofushi, K. Murakami-Murofushi, Biochem, Biophys. Res. Commun. 320 (2004) 1351–1358.
[11] D. Castagnolo, A. De Logu, M. Radi, B. Bechi, F. Manetti, M. Magnani, S. Supino, R. Meleddu, L. Chisu, M. Botta, Bioorg. Med. Chem. 16 (2008) 8587–8591.
[12] T. Rous, E. Pahontu, C. Maxim, R. Georgescu, N. Stanica, G.L. Almajan, A. Gulea, Polyhedron 29 (2010) 757–777.
[13] Y. Zhag, L. Zhang, L. Liu, J. Guo, D. Wu, G. Xu, X. Wang, D. Jai, Inorg. Chim. Acta 363 (2010) 289–293.
[14] F. Caruso, M. Rossi, J. Tanski, R. Sartori, R. Sariego, S. Moya, S. Diez, E. Navarrete, A. Cingolani, F. Marchetti, C. Pettinari, J. Med. Chem. 43 (2000) 3665–3670.
[15] P.F. Liguori, A. Valentini, M. Palma, A. Bellusci, S. Bernardini, M. Ghedini, M.L. Panno, C. Pettinari, F. Marchetti, A. Crispini, D. Pucci, Dalton Trans. (2010) 4205–4212.
[16] J.S. Casas, M.S. Garcia-Tasende, A. Sanchez, J. Sordo, A. Touceda, Coord. Chem. Rev. 251 (2007) 1561–1589.
[17] (a) F. Marchetti, C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 2909–2945;
(b) C. Dendrinou-Samara, L. Alevizopoulou, L. Iordanidis, E. Samaras, D. Kessissoglou, J. Inorg. Biochem. 89 (2002) 89–96.
[18] P.R. Aisen, A.G. Aasa, J. Redifield, J. Biol. Chem. 244 (1969) 4628–4633.
[19] I. Sakıyan, E. Logoglu, S. Arslan, N. Sari, N. Sakıyan, BioMetals 17 (2004) 115–120.
[20] A.S. Thakar, K.K. Singh, K.T. Joshi§, A.M. Pancholi§, K.S. Pandya*, E-J. Chem. 7 (4) (2010) 1396–1406.
[21] K.R. Surati, B.T. Thaker, Spectrochim. Acta Part A 75 (2010) 235–242.
[22] K.R. Surati, B.T. Thaker, C.K. Modi, Russ. J. Coord. Chem. 34 (2008) 25–33.
[23] K.R. Surati, B.T. Thaker, G.R. Shah, Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 38 (2008) 272–279.
[24] K.R. Surati, B.T. Thaker, S.L. Oswal, R.N. Jadeja, V.K. Gupta, Struct. Chem. 18 (2007) 295–310.
[25] K.R. Surati, B.T. Thaker, J. Coord. Chem. 59 (2006) 1191–1202.
[26] K.R. Surati, B.T. Thaker, P. Patel, S.D. Parmar, J. Iranin Chem. Soc. 3 (2006) 371–377.
[27] D.D. Perrin, W.L.F. Armarego, D.R. Perrin:, Purification of Laboratory Chemicals, 2nd ed., Pergamon Press, 1981, pp. 98–111.
[28] A. Gordon, R. Ford, S. Khimika, A Handbook of Practical Data, Techniques and References, John Wiley and Sons, Moscow, 1976, pp. 246, 248–253.
[29] T. Gunduz, N. Gunduz, I. Şakiyan, Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 24 (4) (1994) 519–522.
[30] J.W. David, J.M. Straley, J. Org. Chem. (1961) 3825–3826.
[31] J.M. Andrews, J. Antimicrob. Chemother. 48 (1) (2001) 5–16.
[32] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th ed., Wiley, New York, 1991, pp. 86–89.
[33] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Wiley, New York, 1978, pp. 167, 183–188.
[34] F.P. Dwyer, D.P. Mellor, Chelating Agent and Metal Chelates, Academic Press, New York, 1962, pp. 189–194.
[35] M.R. Rosenthal, J. Chem. Educ. 50 (1973) 331.
[36] J.L. Pascal, J. Potier, C.S. Zhang, J. Chem. Soc., Dalton Trans. (1985) 297.
[37] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
[38] R.A.W. Johnstone, Mass Spectrometry for Organic Chemists, Cambridge University Press, London, 1972.
[39] F.W. McLafferty, Interpretation of Mass Spectra, 2nd ed., The Benjamin/Cummings Publishing Company, Canada, 1973.
[40] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464.
[41] I. Sakıyan, E. Logoglu, S. Arslan, N. Sari, N. Sakıyan, BioMetals 17 (2004) 115–120.
[42] N. Raman, A. Kulandaisamy, K. Jeyasubramanian, Synth. React. Inorg. Met.-Org. Chem. 31 (7) (2001) 1249–1270.
[43] K. Shanker, R.V. Rohini, V. Ravinder, P.M. Reddy, Y.P. Ho, Spectrochim. Acta Part A 73 (2009) 205–211.
[44] D. Rehder, Inorg. Chem. Commun. 6 (5) (2003) 604–617.
[45] L.J. Boucher, H.K. Garber, Inorg. Chem. 9 (1970) 2644–2649.
[46] P.S. Bryan, J.C. Dabrowiak, Inorg. Chem. 14 (2) (1975) 299–302.